

4.7

ETCHING & CLEANING

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4.7 ETCHING & CLEANING

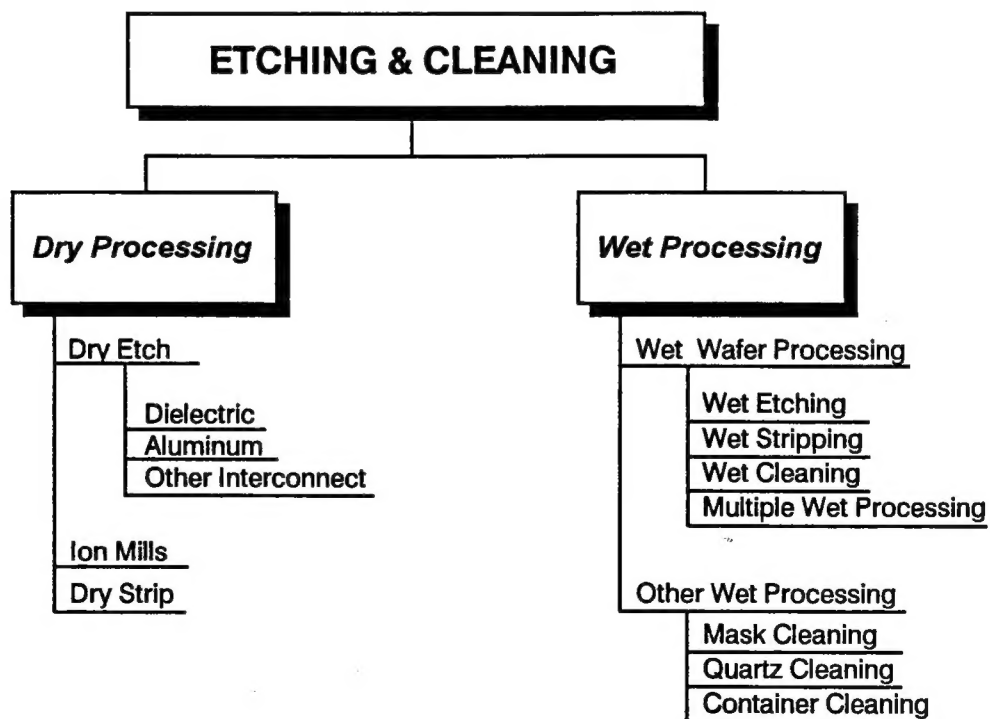


- Dry processing and wet processing are the two major segments in the Etching & Cleaning classification.
- Dry processing methods are chemical processes that use a plasma to etch or strip films.
- Wet processing equipment is used to remove particles and contamination. It is used to clean wafers, masks, containers and quartz elements.

The Etching & Cleaning classifications have been revised with this issue. Dry processing and wet processing now compose the two major segments in this section. Dry etching, ion milling and dry stripping make up the dry processing segment. Wet wafer processing and other wet processing make up the

wet processing segment. Wet wafer processing equipment consists of cleaning, stripping, etching and multiple wet processing systems. Other wet processing equipment includes non-wafer related cleaning equipment such as mask, container and quartz cleaners (see presentation 4.7.0-1).

Presentation 4.7.0-1



Source: VLSI RESEARCH INC
2245-12P

Dry Processing

Dry processing methods are chemical processes that use a plasma to drive the reaction. Dry etching is the major segment of dry processing. Today, virtually all etching processes are dry processes. Typically, a chemical reactive gas, physical abrasion or a combination of the two are used to perform this process. Etching occurs after the resist processing stage. It involves the selective removal of films not covered by the photoresist to form interconnects, contacts and vias. The type of films etched are dielectrics, aluminum, polysilicon and tungsten films.

Several dry technologies are used to etch films. They include planar plasma, reactive ion, magnetically enhanced reactive ion, electron cyclotron resonance, inductive or transformer coupled plasma, high-density reflected electron, helicon wave and ion milling. The numerous variety of film chemistries creates a substantial demand for all of these technologies.

Because of its special characteristics, ion milling is a market unto itself. It is a process that is older than all other plasma methods. Ion mills differ from plasma reactors in that the process is purely physical, there is no chemical reaction. So, it can etch any film. Process wise, ion mills are more closely akin to milling machines, such as those found in any machine shop. This is because the ion beam physically removes all surface material. There is essentially no etching preference (selectivity) between the film being milled and the underlying or masking materials.

Photoresist stripping follows the etch process. Dry stripping completely removes the photoresist with stripping plasmas. Dry stripping systems are similar to plasma etchers in that reactive gases are used to remove unwanted surface layers. Today, dry stripping techniques dominant the strip-

ping market. This is primarily because wet stripping cannot deal with the small geometries, surface hardened resists and heavily implanted resists routinely encountered in today's semiconductor processing.

Wet Processing

Wet processing equipment is used to remove particles, contamination and other material from the wafer, mask, quartz products and containers used in the semiconductor manufacturing process. Wet processing consists of wet wafer processing and other wet processing. Cleaning equipment makes up most of the wet wafer processing market. There are various methods used in cleaning wafers. These methods are RCA clean, scrubbing, spray clean, vapor phase clean and dry clean.

Wet wafer processing also includes wet stripping, wet etching and multiple wet processing. Wet stripping involves the complete removal of layers, etch barriers and implant barriers. With wet stripping, a mixture of some acid together with hydrogen peroxide is used to remove resist masks from a wafer. Wet etching entails the selective removal of materials to form interconnects, contacts and vias. In wet etching an aqueous acidic solution is used to dissolve thin-films, silicon, etc., thus making trenches in the substrate. In multiple wet processing, a combination of etching, stripping and cleaning methods are combined into one system.

Other wet processing includes mask cleaning, quartz cleaning and container cleaning. This equipment removes impurities from the mask, quartz products and wafer containers, respectively. Mask cleaning is similar to wet wafer cleaning. Reticles are cleaned using methods similar to wafer cleaning to eliminate surface contaminants. The reticles are then rinsed and spin dried or IPA vapor dried.

Quartz cleaning is used for bell jars, CVD diffusion tubes and other miscellaneous quartz products used in wafer processing. In the container cleaning method, carriers

and boxes for silicon wafers are washed in a chemical solution. They are then rinsed in DI water and spin dried or blow dried to remove particles and contaminants.

Notes

CURRENT INDUSTRY CHARACTERISTICS

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4.7.1 CURRENT INDUSTRY CHARACTERISTICS



- Various etcher technologies are on the market today.
- Line width decreases into the submicron range have driven the industry to improve wet processing.
- Enclosures, automation and microcontroller-controlled-systems have resulted in equipment improvements.

There are various etcher technologies on the market today. These fall under two categories: high pressure systems and low pressure systems. The high pressure systems operate at or greater than 50 mTorr and are used for the production of devices that require greater than half-micron geometries. Low pressure devices operate at less than 50 mTorr and are used for the production of devices that require less than half-micron geometries. The high pressure technologies include conventional planar plasma systems, reactive ion etching (RIE), and magnetically enhanced reactive ion etching (MERIE). The low pressure technologies are electron cyclotron resonance (ECR), helicon wave, inductively or transformer-coupled plasma, and high-density reflected electron (HRe).

As R&D into submicron geometries continued, conventional plasma etch, RIE and MERIE technologies exhibited limitations due to localized etch effects, or microloading. With microloading the etch rates and profiles vary in areas with different pattern densities. Research engineers discovered that low pressure operation minimized microloading. In addition, they found that low pressure (less than 20 mTorr) and high density features in etch systems are necessary elements for submicron production of

DRAMs and other ICs. However, conventional plasma, RIE and MERIE systems were unable to accomplish low pressure, high density features. At low pressures the etch rates are low. To increase etch rates, plasma enhancement is required. ECR was a form of plasma enhancement which incorporated low pressure, high density technologies. However, researchers focused on other technologies which could accomplish these features. Some other ways of plasma enhancement are inductively or transformer-coupled plasma, HRe and helicon wave. All of these systems operate at pressures below 10 mTorr.

Inductively coupled plasma technology uses two parallel plates inside the etch chamber. The plasma is generated between the plates by an inductive coil. The inductive coil is attached vertically to both sides of the chamber wall. Another inductively coupled type system is called transformer coupled plasma (TCP). TCP also uses a coil to generate the plasma between two parallel plates. Although, with the TCP design, the coil is placed horizontally above the wafer.

HRe technology is capacitively coupled and uses three electrode plates. Two of the plates are horizontal while one is vertical. The plasma is created within the three

plates. This technology uses a magnetic field to contain the plasma. Permanent magnets are mounted around the outside of the etch chamber to create a magnetic field inside the chamber.

The helicon wave also uses inductive coupling. In this, a high density plasma is generated within a quartz tube by an inductor wrapped around it. The region where the plasma source is created is in a separate area of the tube, away from the wafer.

With device critical dimensions at the sub-micron level, the cleanliness of a wafer surface has become very important. The increased importance of removing ever smaller contaminants is placing renewed emphasis on the entire wet wafer process. Surface contamination on silicon wafers is a very large concern. Particulates on the surface are directly responsible for low yields in the industry. Thus, the industry is driven to improve both wet processing techniques and performance. Conventional batch methods can no longer adequately meet the cleanliness requirements essential for submicron manufacturing. Cross-contamination occurring in the batch process limits its performance.

Major improvements on equipment which have resulted in less wafer contamination are self enclosed, automated, microcontroller controlled systems. An important step toward enclosed manufacturing systems is the cluster tool concept. With this concept, the wafer is contained in a controlled atmosphere between critical process steps. Contamination is reduced because wafer handling is lessened. In addition, wafer exposure to potentially contaminating atmosphere is diminished.

Another issue which has been brought up is the environmental impact of wet chemical waste. Concerns about effects on the environment from wet chemical waste is reducing wet chemicals' usage. However, chemical consumption has increased due to the increase in wafer diameter. Therefore, process steps to further reduce or eliminate wet chemicals are being investigated. For example, with parallel plate strippers, only a DI water rinse after the strip process is needed. Two cleaning technologies that were developed to reduce or eliminate the wet portion of the cleaning procedure were vapor phase and dry cleaning technologies. However, both technologies still need a wet rinse to remove all particle contaminants.

4.7.1.1 Development of the Etching and Cleaning Industry



- The stimulus for the evolution of dry etching systems has been the continual decrease in linewidth geometries.
- Newer dry etch developments are directed at low pressure, high density plasma.
- No cleaning method has been able to displace the RCA clean.
- Vapor phase cleaning and dry cleaning methods reduce wet chemical usage. However, they do not clean as well as other wet cleans.

The etching and cleaning industry grew out of the earliest developments of the semiconductor process. Historically, both etching and cleaning activities dealt with chemicals and chemical baths. These baths consisted dominantly of acid etches and cleans. As such, there was no real equipment market. Instead, both etching and cleaning were done in inert sinks beneath fume hoods, similar to those found in a home kitchen. These sinks and hoods eventually developed into entire work stations. Each work station contained an etching sink, a cleaning sink and a rinsing sink, all under one hood. Over time, the work stations developed still further into cleaning and etching systems containing automatic temperature controls and wafer feeding mechanisms.

In semiconductor device manufacturing today, the dry etching process has become predominant. The catalyst for dry etching has been continual decreases in linewidth geometry. As linewidth requirements shrank, wet processing equipment was unable to provide useful etches because the liquids could not get into the trenches. Dry etching overcame this problem by allowing the reacted gas to escape from the trenches, thereby allowing fresh gas to continue etch-

ing. As a result, today, only a minimal amount of etching is done using wet techniques. Dry etching has other advantages over wet processing. For one, dry etching is cleaner. For another, it is more selective. Wafers do not have to be dried, and it eliminates the need for hazardous wet chemicals as well as for their disposal. However, wet chemistries are the most effective method for particle removal. Therefore, semiconductor manufacturers continue to use wet processing methods for most cleaning procedures.

Cleaning also gained substantial attention as linewidths approached the submicron level. Finer geometries required cleaner wafers. Semiconductor manufacturers incorporated a multitude of cleaning steps, each with different solutions, to ensure removal of contaminants. Also, environmental concerns of wet chemical waste brought about the need to reduce or eliminate wet chemicals. As a result, the demand for spray cleaning equipment increased since this type of equipment required fewer chemicals. In addition, newer cleaning methods using little or no wet chemicals were introduced. These methods were vapor phase, and dry cleaning.

Stripping is also a cleaning process. Ashing equipment was the original name for stripping equipment because the plasma used during stripping reduced the photoresist to ash. It was out of these early stripping systems that today's dry plasma etching techniques emerged.

4.7.1.1.1 Development of the Dry Etching Equipment Industry

1970's

The origination and development of plasma etching occurred between 1968 and 1972. In the late sixties, Steven Irving at Signetics Corporation performed some of the earliest research work in plasma etching using Tracerlab's LTA-600J. Irving's patent on the gas plasma vapor etching process contained the essential details of modern day barrel plasma ashing (stripping) methods containing CF₄ and O₂.

Irving soon left Signetics to join a young company called International Plasma Corporation. While there Irving and Richard Bursin built one of the first plasma etchers designed specifically for this industry. International Plasma Corporation later became Branson IPC, and is now a part of GaSonic. Separately, Horsley and Jacob of LFE International Plasma, were pioneering plasma etching on the east coast. They developed the first plasma process for etching silicon nitride.

Jacob's patent on 'process and material for manufacturing semiconductor devices' addressed the etching of silicon dioxide, silicon nitride, poly-crystalline silicon and refractory metals. Irving's and Jacob's patents established the basis for plasma etching, as well as plasma ashing. This occurred in 1972.

Initially, plasma technology was slow to take off. By 1975 the market had reached a mere \$1.6M (see presentation 4.7.1.1.1-1). Semiconductor engineers did not fully understand plasma technology. Steve Irving once said, "Many engineers he visited during this period thought that a plasma etcher was for medical applications."

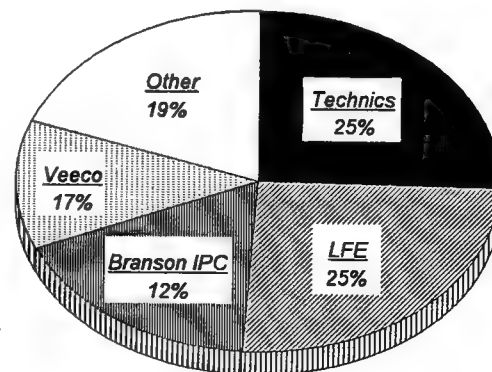
Nevertheless, the plasma industry began to take hold in the mid-seventies. The first commercial application was for etching silicon nitride films on LED devices. As silicon nitride uses spread to other more common device processes, plasma etching spread to other device types. The first was microwave transistors, and then beam lead devices. These preliminary successes, coupled with wet chemical etching difficulties, created strong pressure to find new ways to implement plasma etching.

The emergence of LSI ICs in the mid-seventies provided the primary push for the widespread introduction of plasma etching. The hot-phosphoric wet chemical etch that was used at the time was extremely difficult to control. Additionally, polysilicon was be-

Presentation 4.7.1.1.1-1

Dry Etch Equipment Market as It Existed in 1975

(total sales = \$1.6M)



Source: VLSI RESEARCH INC
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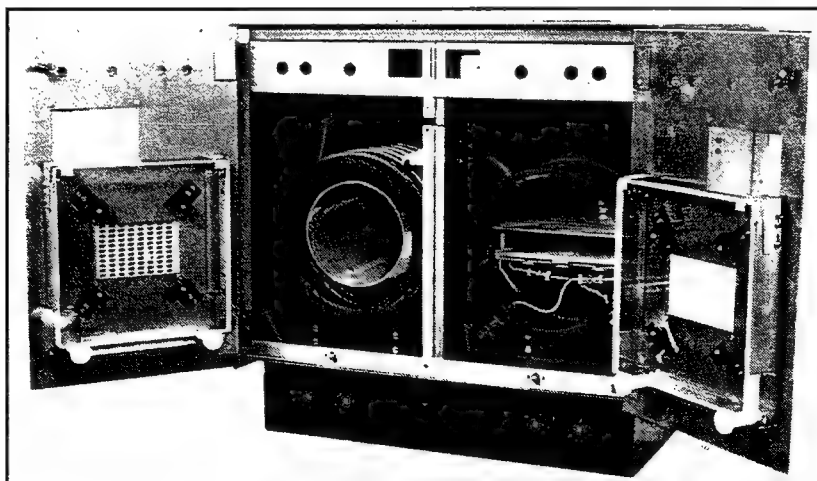
ginning to be used for gates. The barrel plasma etcher, shown in presentation 4.7.1.1.1-2, was quite adequate for etching silicon nitride. Barrel etchers were batch systems that used a cylindrical configuration. The barrel plasma etcher required a gaseous chemical etchant and an energy source. The architecture of a barrel plasma etch system consisted of a chamber, a gas supply, a vacuum system and an RF power supply (see presentation 4.7.1.1.1-3). Simple barrel plasma etchers had certain characteristics that limited their usefulness. Among these limitations were isotropic (non-directional) etch, poor wafer uniformity, and excessive radiation damage. In addition, barrel etchers were poor for etching five micron polysilicon gates, the linewidth of the day. Thus, an improved etching method was needed to control critical dimensions for this as well as for silicon nitride and polycrystalline silicon films.

Designers of barrel systems tried to minimize these problems by developing better control of process parameters and by emphasizing processes that could tolerate significant over-etching. Designers of barrel etchers also attempted to minimize radia-

tion damage by incorporating perforated metal shields to isolate wafers from the high-energy RF field. The result was that only electrically neutral reactant plasma species could reach the wafer's surface. However, these improvements were not sufficient to overcome all the difficulties. Consequently, today barrel etchers are mostly used for stripping films.

In 1973, Alan Reinberg at Texas Instruments abandoned the barrel etcher concept and invented the parallel plate reactor. This reactor paved the way for modern dry etching of polysilicon. It also foreshadowed future developments needed to etch silicon dioxide and aluminum. As a result, this improvement made possible the production of LSI ICs. Moreover, it also provided the basic technology for a complete dry etched process line. It was an exciting time as many breakthroughs, including plasma deposition and plasma photoresists pushed the technology into new areas.

ET Systems (Electrotech) introduced the first commercial planar plasma etcher in 1975. The system was a rather crude model of a diode sputtering system. The elec-



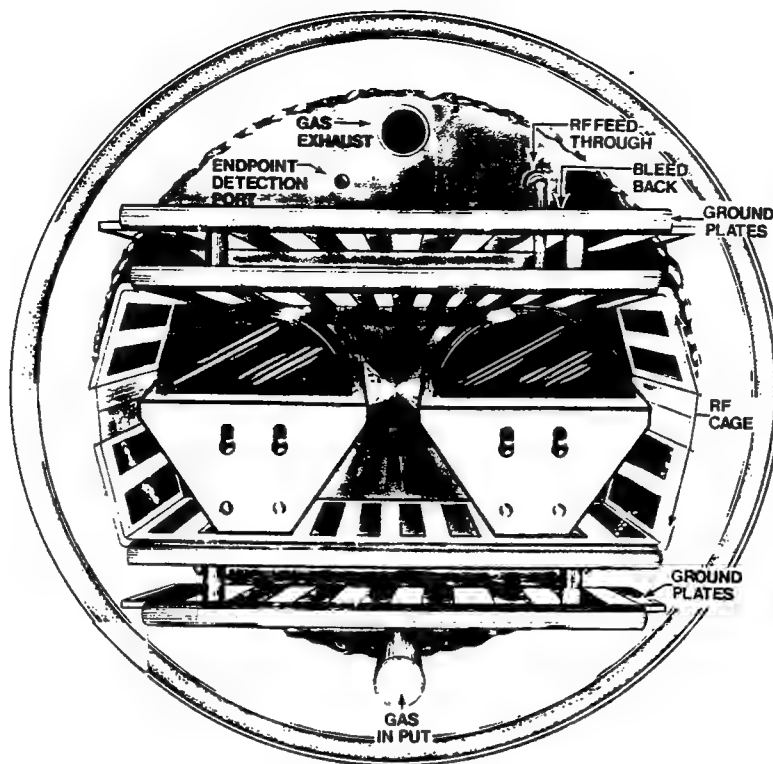
Source: LFE
2245-16

Presentation 4.7.1.1.1-2

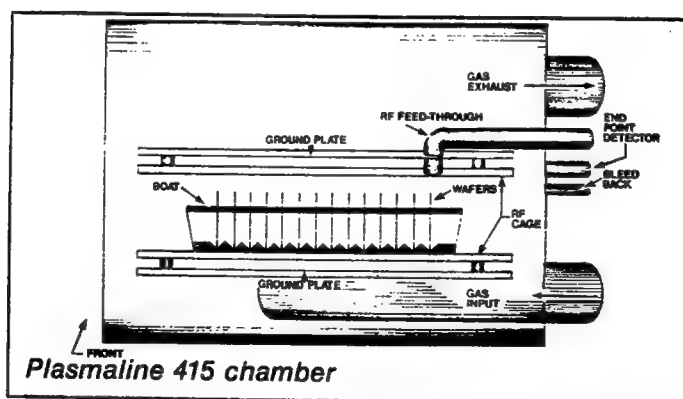
LFE's 1002 Barrel Etch System

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4.7.1 5



Plasmaline 415 chamber with wafer carriers



Plasmaline 415 chamber

Source: Tegal
2245-32

Presentation 4.7.1.1.1-3

A Barrel Plasma Etch Chamber

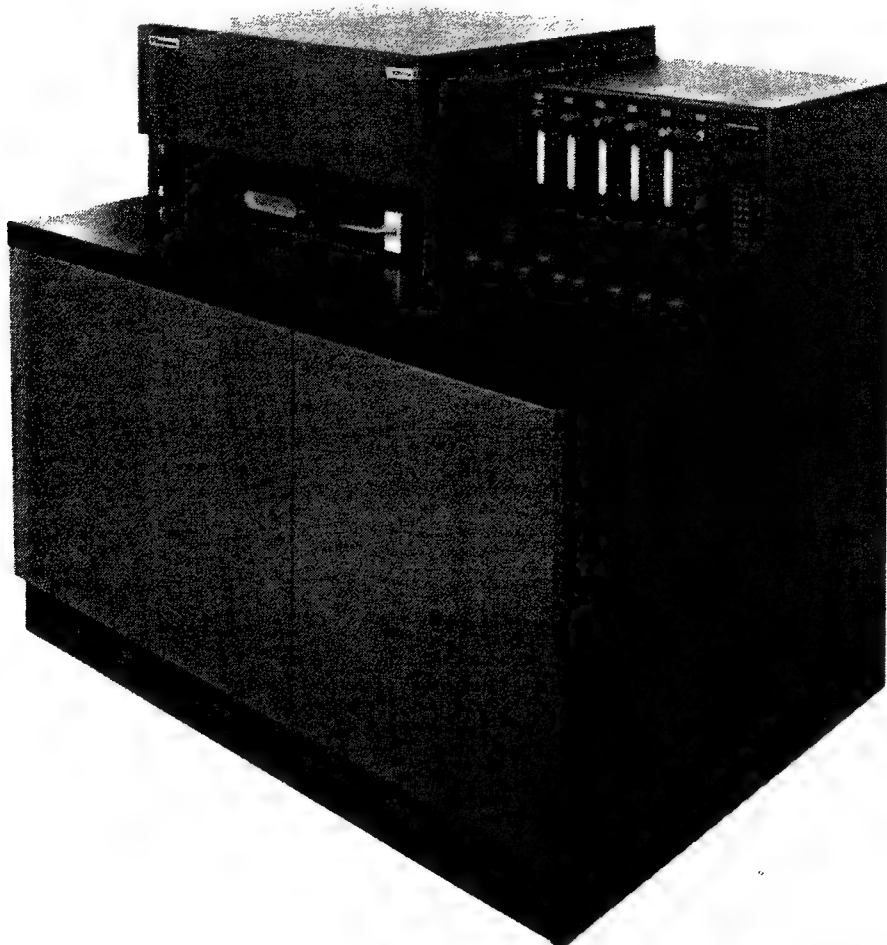
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trodes were placed inside the reaction chamber and the wafers were placed flat on one electrode. Presentation 4.7.1.1.1-4 shows ET System's planar plasma system as it looked in the late seventies.

Planar plasma reactors operated on essentially the same principle as did barrel plasma etchers. However, planar plasma etchers displayed major process advantages over barrel etchers. They offered better CD control for etching polysilicon gates. Uniformity and anisotropy were much better since the plasma was directed towards the wafer in planar reactors. They had good selectivity and better control over the etch-

ing ions. This greater control resulted in better uniformity across each wafer as well as between wafers. These machines etched silicon more slowly than they etched silicon dioxide. This was directly opposite to the etch ratios achieved for these same materials in a barrel reactor.

These benefits led to new single wafer system configurations that significantly changed the plasma etching market as the seventies ended. The single wafer systems introduced by Tegal and Tokyo Ohka Kogyo obsoleted the older batch operated systems (see presentations 4.7.1.1.1-5 and 4.7.1.1.1-6). Tegal's Plasma Inline 700 pro-

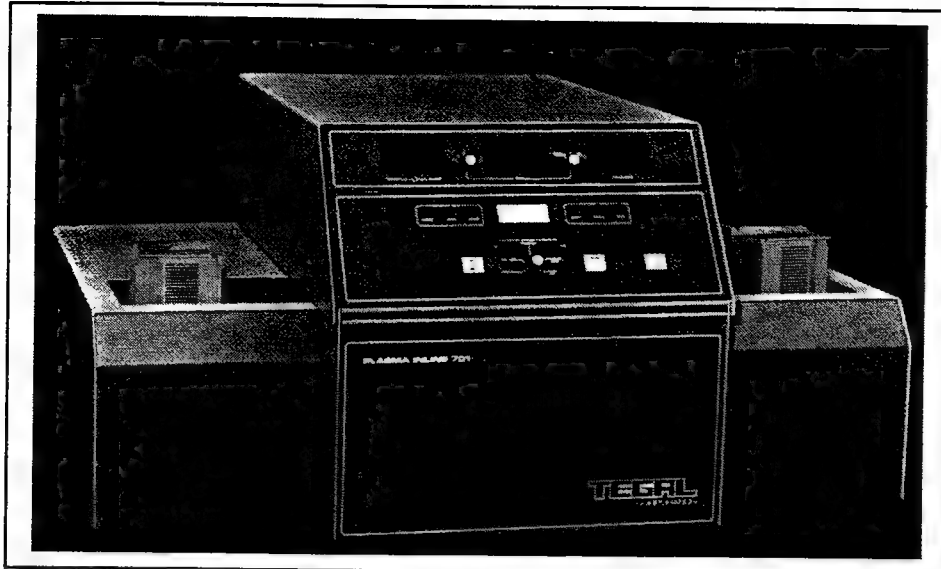


Presentation 4.7.1.1.1-4

Source: ET Systems, Inc
2245-17

ET Systems' Plasma Fab 425

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Source: Tegal
2245-18

Presentation 4.7.1.1.1-5

Tegal's Plasma Inline 701



Source: Tokyo Ohka Kogyo
2245-19

Presentation 4.7.1.1.1-6

Tokyo Ohka Kogyo's OAPM-301B Plasma System

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vided single wafer processing for isotropic etching. The Plasma Inline 701 featured anisotropic etching with dimensional control, optical emission and DC bias end point detection. The then current market leaders, Branson/IPC and LFE failed to capitalize upon this shift. They were working on aluminum and oxide etching, which would prove to be a fruitless search for several more years.

1980s

As a result, Tegal emerged as the major player in the United States, while Tokyo Ohka Kogyo became the leader in Japan. The face of the market had completely changed by 1981 (see presentation 4.7.1.1.1-7). Both companies based their success upon providing more uniform polysilicon etches. This increased uniformity provided by these single wafer systems allowed semiconductor manufacturers to push polysilicon linewidths down to its material limits.

Another form of etching, ion milling, also captured enthusiasm between 1979 to 1981 because these systems could etch any material. At the time, ion milling's major area of application was for manufacturing bubble memories. This was because plasma etchers could not etch the thin films used in bubble memories. However, the bubble memory market never materialized, this led to the decline of volume applications for ion mills. These systems are also used to etch gallium arsenide circuits, electron beam masks and multi-layer silicides. Even so, ion mills have found little use in mainstream semiconductor applications. This is because of low throughput, high wafer surface temperatures and their tendency to over-etch, creating 'trenches' in the lower substrate and their tendency to splatter, creating ridges along the milling path.

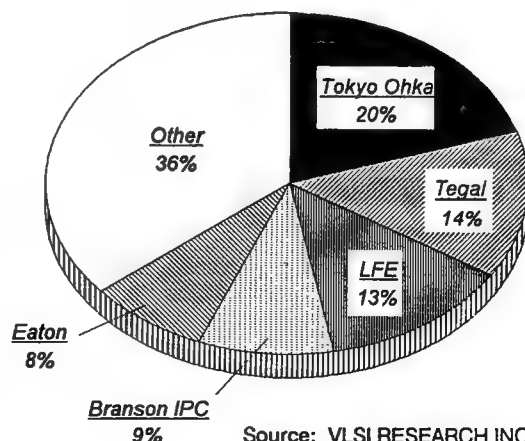
As the industry moved into the 1980's, the advent of 64K DRAM technology brought about a new period of rapid advancements.

This created the need to etch geometries below two microns which meant that all layers would eventually be plasma etched. It presented a new market opportunity. Virtually everyone recognized the growth potential of the plasma etch market. In fact, the etch market went from \$71.8M in 1980 to \$392.6M in 1984, a 52.9% compound annual growth rate. This potential attracted leading equipment companies and venture capitalists. Top design engineers were hired at unusually high yearly salaries. Art Zafiropoulo left LFE, and took a team of design engineers with him to found Drytek. David Lam was lured away from Hewlett-Packard to found Lam Research (he was a protege of Alan Reinberg). Eaton acquired Davis and Wilder and hired John Zajack away from ET Systems (he was a protege of Steve Irving). Perkin-Elmer corralled Reinberg, Irving and Bursin to accomplish a design that is today the basis of Lam Research's oxide process. Applied Materials hired Dan Mayden and David Wang from AT&T. By 1983, there were over sixty companies either already in the market, or planning to enter it.

Presentation 4.7.1.1.1-7

Dry Etch Equipment Market as It Existed in 1981

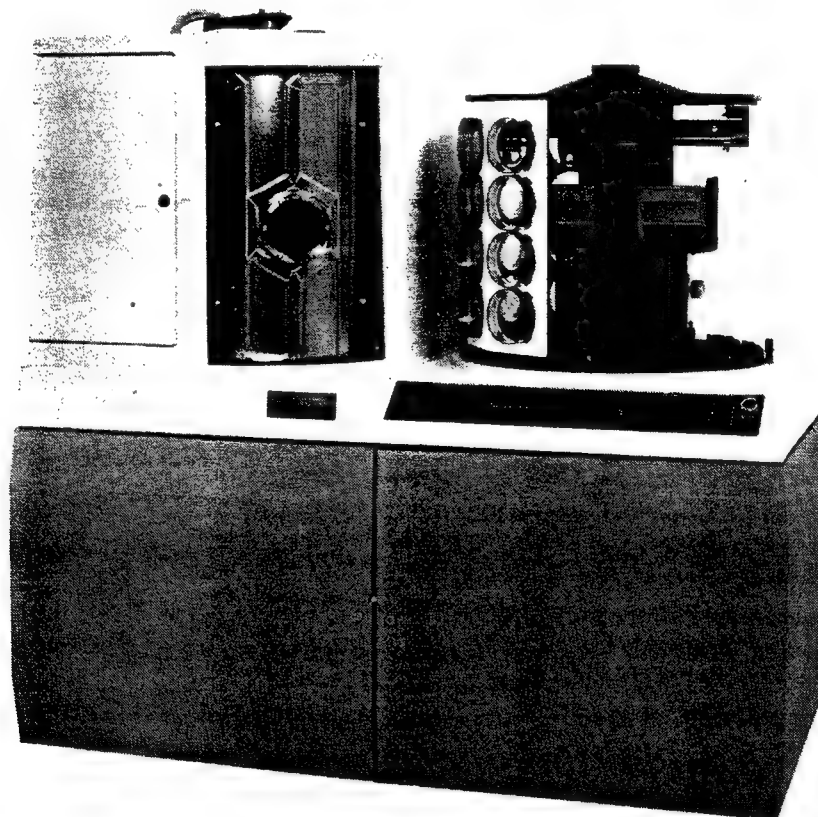
(total sales = \$71.8M)



Source: VLSI RESEARCH INC
2245-20G

Applied Materials' entry into the market proved to be the most successful. The company had licensed Bell Lab's Hex Reactor design for epitaxy. Dan Mayden and David Wang had modified one of these epi reactors to run experiments in RIE etching at AT&T. The results were better than any plasma process available at the time. Applied happened on this, during a normal customer visit to AT&T. They quickly recognized the value and brought both Mayden and Wang to Applied to develop a production version. In 1981, Applied Materials introduced the first production-worthy oxide etcher, the AME 8100 series plasma etch system. Applied introduced this system over a year in advance of any other competition (see presentation 4.7.1.1.1-8).

At the time, this system worked in manner contrary to all the conventional wisdom about what a plasma etcher should be. It was a batch system selling for \$500K at a time that single wafer systems were the most favored and were priced below \$200K. However, it had one overriding feature: the system worked. It provided uniformly etched oxides for production and did so without sacrificing throughput. Bell Labs' name, coupled to the efficacy of the system, turned the industry topsy-turvy. At the time, companies were demanding single-wafer, load-locked etch systems. However, many companies immediately turned to the machine even though it was not a single wafer and not a load-locked system. To place this in a market context, Applied



Source: Applied Materials
2245-21

Presentation 4.7.1.1.1-8

Applied Materials' AME 8100 Plasma Etch System

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Materials' total plasma etch sales were less than \$3M in 1980. By 1982, Applied Materials had become the market leader. It would be a full year before any other competitor could duplicate a production worthy oxide etcher.

Perkin-Elmer's Omni-Etch model 10000, was to be the first viable single wafer oxide etcher (see presentation 4.7.1.1.1-9). However, it was a year too late to market and it was plagued with mechanical reliability problems. This doomed it to relative obscurity. Perkin-Elmer exited the dry etch market in 1987. In early 1989, Lam Research bought Perkin-Elmer's process technology. Lam Research used Perkin-Elmer's unique low frequency discharge process concept as the basis for the Rainbow 4500 oxide etcher.

Lam Research entered the market with a strategy for providing production tools that were extremely reliable and that would work on a day-to-day basis. This strategy guided them to becoming one of the market leaders with their workhorse, the Auto Etch 450 (see presentation 4.7.1.1.1-10).

Applied Materials marketing strategy created a fundamental shift in responsibility between buyer and seller during the early eighties. Before this, equipment manufacturers sold only hardware. The responsibility for making a process work rested solely in the hands of the buyer. This was becoming very costly and very problematic. One leading semiconductor manufacturer complained at the time that it had some fifteen process

engineers working on just an aluminum process, and with little success. Applied Materials changed this by guaranteeing a working process with their AME 8100 series. They were the first in the industry to guarantee etch rate, linewidth uniformity, selectivity and up-time of the system.

Applied was making major market share gains by focusing on the advantages of offering a working process. However, most of the other etch companies had focused upon which dry etch mechanism to use. Several alternate methods for planar dry etching had developed. Among these were reactive ion etching (RIE). Physical processes (sputtering) gave new advantages to etching in addition to those achieved with the purely reactive chemical processes of



Source: Perkin-Elmer
2245-22

Presentation 4.7.1.1.1-9

Perkin-Elmer's Omni-Etch 10000



Source: Lam Research
2245-23

Presentation 4.7.1.1.1-10

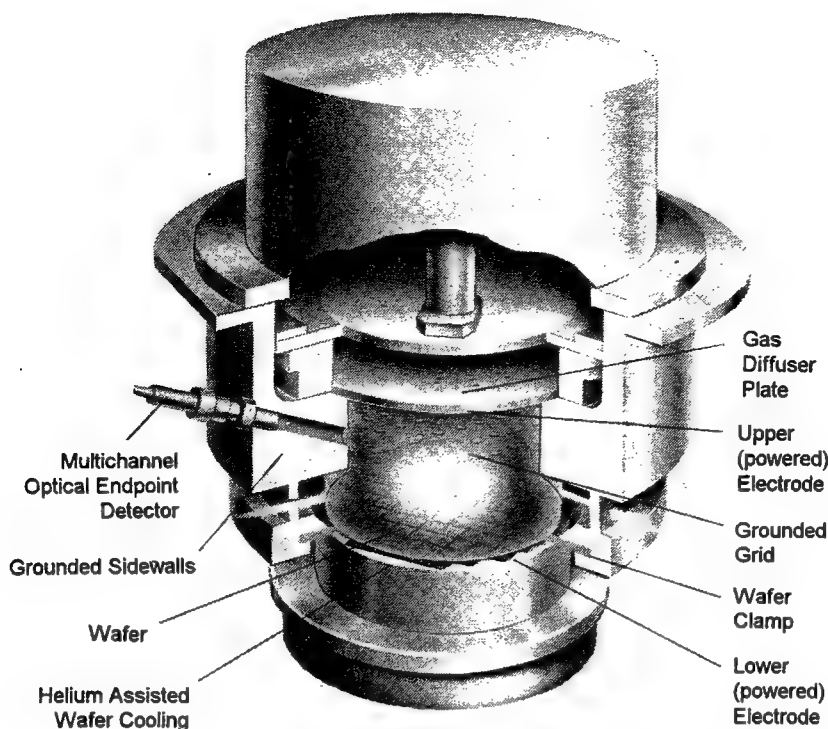
Lam Research's Auto Etch

plasma etching. So, the terms RIE and RIBE evolved. They were often used interchangeably with the term planar plasma etchers. This was because the equipment used was often virtually identical and could be easily altered to do other processes.

RIE systems were excellent for etching silicon dioxide that had been deposited over a silicon layer. These systems typically operated with a selectivity ratio of 35:1 in comparison to 10:1 for conventional plasma etching systems. RIE systems also offered advantages for certain types of aluminum etch processes. This was because the physical nature of the process aided in the removal of copper.

Aluminum etching was another area of hot activity for Applied Materials. Applied gained an advantage by focusing on production worthy processes. In 1979, Davis and Wilder showed the first etching of aluminum using dry processes. However, it never worked in production. By 1982, Applied Materials and ET Electrotech were performing aluminum etching. ET Electrotech was probably the first to etch aluminum on R&D pilot lines. However, these early systems required a high degree of engineering to operate properly. Applied Materials was the first to consistently etch aluminum in production. This advantage quickly made Applied Materials the market leader in aluminum etching.

In comparison to plasma etching, RIE methods usually had somewhat lower etch rates. RIE was not as good for etching polysilicon on gate oxides. This was due to radiation damage to the oxide and a tendency for undercutting. Since both plasma and RIE processes had strengths and weaknesses, some equipment manufacturers developed systems that were hybrids of the two processes, called triodes. In triode systems, conventional plasma etching and RIE etching could be performed simultaneously. GCA had successfully developed the triode system along with a dry rinse and bake system to successfully etch the multilevel sandwich metal structures TiW-Al-TiW. In 1988, General Signal merged GCA's triode technology into Drytek after the GCA-General Signal merger. Presentation 4.7.1.1.1-11 shows Drytek's 384T triode model. This technology now belongs to Lam Research, after Lam bought Drytek in 1993.



Source: Lam Research
2245-44D

Presentation 4.7.1.1.1-11

384T Triode Etch Chamber

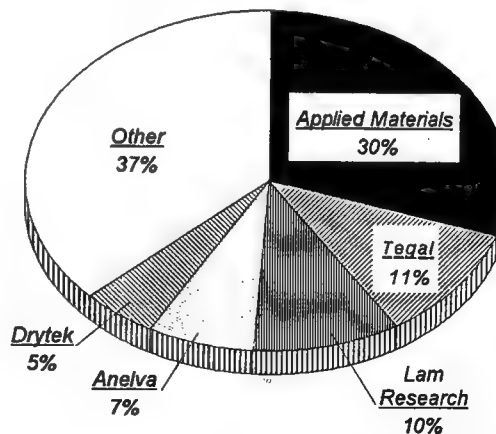
The market battles settled by 1985. Tegal was the only company from the previous generation with the staying power to have lasted. Applied rose from nowhere to the top based on process capability. Lam rose to third place with a strategy focused on reliability. Anelva focused on its parent, NEC and the Japanese market. Drytek made it to the fifth spot by being the first to use the cluster tool concept (see presentation 4.7.1.1.1-12).

As the market settled down, the focus again turned to R&D. This led to new technologies. Plasma etching could not produce the required anisotropic profiles and RIE created ion induced damage to the gate oxide. Both technologies caused electron damage and UV light damage. RIE systems also have a slow etch rate. This is due to the need to operate at reduced pressures. Low etch rates forced RIE etcher manufacturers to use batch reactors. With batch reactors,

Presentation 4.7.1.1.1-12

Dry Etch Equipment Market as It Existed in 1985

(total sales = \$295.1M)



Source: VLSI RESEARCH INC
2245-24G

many wafers could be etched simultaneously, thereby increasing effective process throughput. Magnetically enhanced reactive ion etching (MERIE) was developed in response to the need to improve RIE etch rates and reduce self-biasing. In addition, MERIE allows the full benefits of the RIE process in a single wafer reactor. MERIE uses the same basic technology as RIE systems, but the intensity of the plasma is increased by the use of a magnetic field. The magnetic field is applied perpendicular to the electric field and parallel to the wafer's surface. This technique increases etch rates, selectivity and uniformity at low pressure, while promising to lower damage. However, MERIE had some problems. One was that the high plasma densities caused dopant depletion in silicon. Another was the combination of the magnetic and electric field at the wafer resulted in a nonuniform plasma. To compensate for this nonuniformity, the magnetic field was rotated. However, rotating the magnetic field damaged the wafer.

Technologists continued to investigate other etch techniques. One technique examined was electron cyclotron resonance (ECR). Oakridge National Laboratories had originally developed ECR sources in the late fifties for use in fusion. The design incorporates a microwave frequency plasma source. This source creates an intense plasma in a separate cavity region and can be remote from the wafer position. The etchant ions are extracted from this plasma and focused onto the wafer surface.

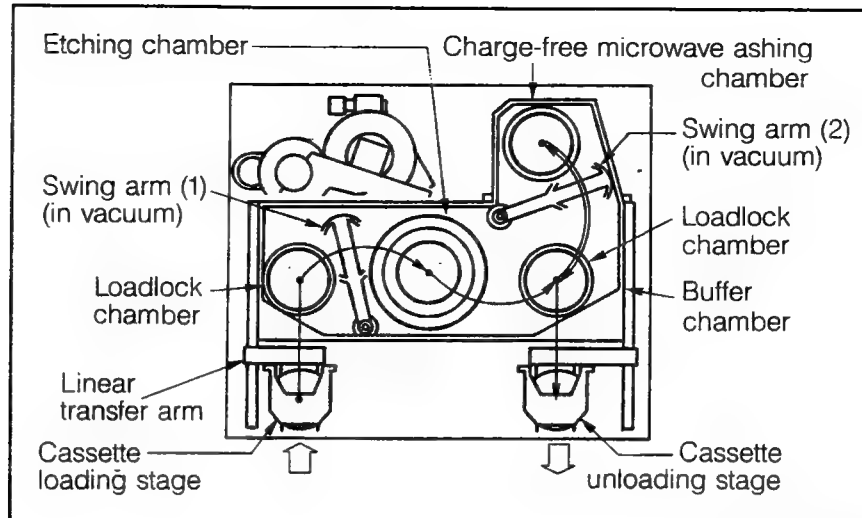
ECR technology was further developed in Japan. In 1982, NTT was the first to patent an ECR source for use in semiconductor equipment. In 1987, NTT licensed its ECR patents to Sumitomo Metals, Anelva, Hitachi and MRC (see presentation 4.7.1.1.1-13). However, in mid-1988, Anelva suspended marketing of its ECR system in the United States because of technical problems.

In early 1989, Veeco Instruments Group introduced its patented ECR plasma source. This design was for UHV and reactive gas operations. About the same time researchers at Michigan State University developed and patented a unique, large-aperture ECR source. Wavemat, a small start up company in Michigan later licensed this patent.

1990s

In 1990, Sematech funded Oakridge National Laboratories to do further research into ECR applications for semiconductor plasma etching. At this time, ECR was thought to be the successor to plasma source technology. However, as more research on ECR was done, less faith was put into ECR. More problems than advantages were associated with it. One problem was that ECR was complex. Another was that it was difficult to achieve uniform etch rates across the entire wafer. In addition, there were microloading problems with 200 mm wafers. By mid-1991, many etch equipment manufacturers were disappointed with ECR and chose to seek alternate technologies. Hitachi was the only company with a high success rate with its ECR etch system.

As R&D continued into the submicron geometries, conventional plasma etch, RIE and MERIE technologies exhibited localized etch effects, or microloading. With microloading, the etch rates and profiles varied in areas with different pattern densities. Research engineers discovered that low pressure operation minimized microloading. In addition, they found that low pressure (less than 20 mTorr) and high density features in etch systems are necessary elements for submicron production of DRAMs and other ICs. However, conventional plasma, RIE and MERIE systems were unable to accomplish low pressure, high density features. ECR incorporated low pressure, high density technologies. Regardless, research-



Source: Hitachi
2245-26

Presentation 4.7.1.1.1-13

Hitachi's M-328EX/SX ECR Configuration

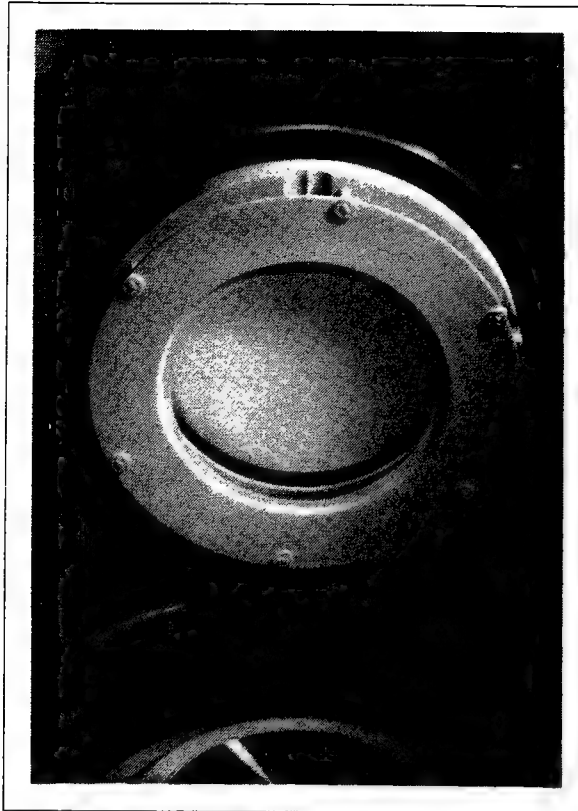
ers focused on other technologies which could accomplish these features. These technologies were inductively coupled plasma, high-density reflected electron (HRe) and helicon wave.

Inductively coupled plasma was originally developed in the late eighties. However, in 1993, Applied Material's was the first company to come out with an etch system employing inductively coupled high density plasma (HDP) technology. This system was the Centura HDP. This technology uses two parallel plates inside the etch chamber. The plasma is generated between the plates by an inductive coil which is attached vertically to both sides of the chamber wall.

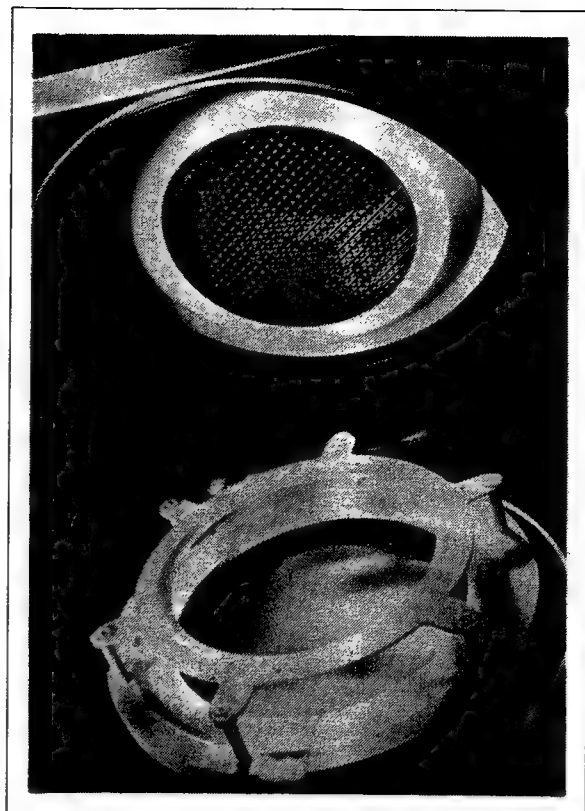
Another inductively coupled type technology is transformer coupled plasma (TCP). LAM research developed this technology in 1992 (see presentation 4.7.1.1.1-14). The TCP systems also use a coil to generate the plasma between two parallel plates. Although, with the TCP design, the coil is placed horizontally above the wafer. The

advantages of HDP and TCP are better CD control, minimal microloading, no radiation damage, and low foreign matter and particle contamination.

Tegal developed HRe technology. The HRe system uses Tegal's patented triode configuration. This technology uses a magnetic field to contain the plasma. The magnetic field is limited to the wall area of the reactor. The magnetic field acts like a physical barrier from the etch chamber wall, much like a container inside of a container. Since the chamber is essentially untouched by etchants, the physical parts inside the etch chamber are spared any damage. Therefore, Tegal guarantees all the parts inside the etch chamber. This is the first time any etch company has guaranteed these parts. Typically, parts inside the etch chamber wear out quickly, since they are etched along with the wafer. So, they are considered consumable and have to be replaced. The monthly cost to replace an etch chamber can be extremely costly. However, with Tegal's HRe design, the plas-



**Lam Research's TCP 9600
Metal Etch Chamber**



**Lam Research's TCP 9400
Polysilicon Etch Chamber**

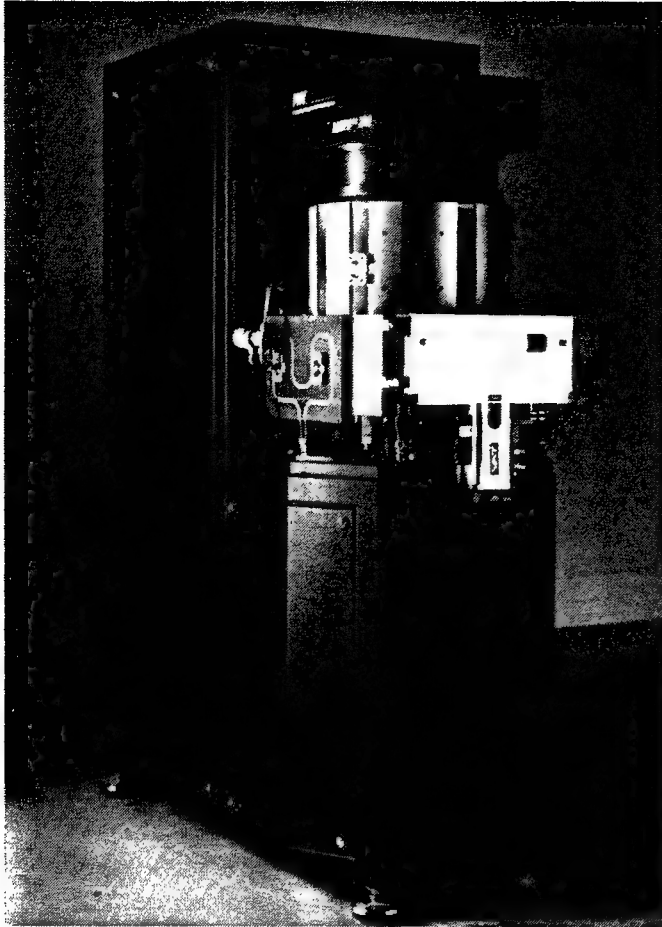
Presentation 4.7.1.1.1-14

Source: Lam Research
2245-25

ma is contained inside the magnetic field, never touching the chamber wall nor the parts inside the chamber.

The helicon wave was developed by Lucas/Signatone and Plasma & Materials Technology (PMT). With this technology, high-density plasma is generated in a source area away from the wafer. The plasma is ignited in the source area by a powered antenna wrapped around a quartz tube, thus producing a helicon wave. The plasma is then guided toward the wafer by an electromagnetic field. PMT calls its helicon technology MORI. PMT has licensed the MORI technology to Anelva and Canon (see presentation 4.7.1.1.1-15).

Clusterable etch systems were also becoming popular by the 1990's. The cluster tool concept was an important step toward closed manufacturing systems. The wafer is kept enclosed in a controlled atmosphere between critical process steps. Cluster tools have multiple, modular, process chambers and a central wafer transport chamber that is usually under vacuum and contains a robotics handler. The modular chambers may consist of any combination of etch, CVD, PVD, RTP, photoresist strip and clean processes. The former Drytek (which Lam Research bought in 1993) invented and patented the cluster tool configuration. However, Applied Materials was the first to



Source: Plasma & Materials Technology
2245-28

Presentation 4.7.1.1.1-15

PMT's MORI 2000 Etch Module

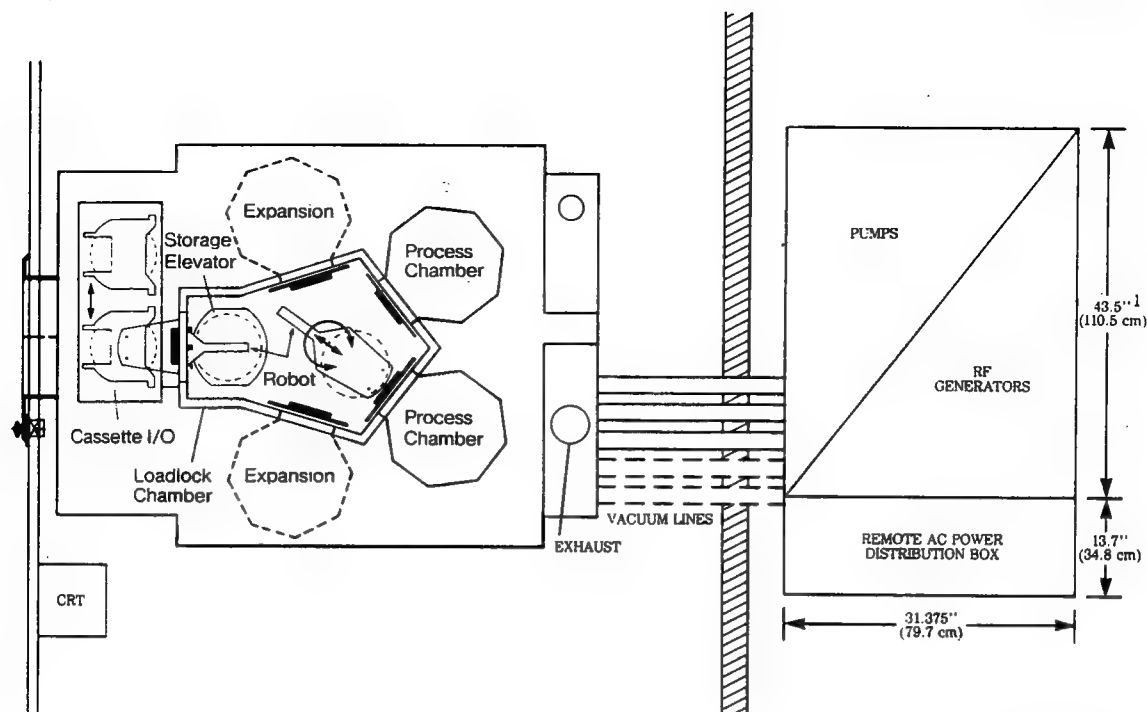
successfully commercialized them. Presentation 4.7.1.1.1-16 illustrates Applied Material's first cluster tool, the Precision 5000. Two main advantages that cluster tools offer are improved process control and lower defects. The processes within the cluster tool are standardized. Therefore, the manufacturers have more control of the processes. Defects are lowered because the wafer is not exposed to contamination from the atmosphere or from people.

Cluster tools were adopted by many equipment manufacturers. Therefore, SEMI Modular Equipment Standards Committee (MESC) decided to set standards on clusterable equipment. These standards specified how the central wafer transport chamber and the modular process chambers connect and communicate. The advantage of standardizing cluster tools is reduced capital equipment costs. Several etch equipment companies adopted the MESC standard. However, most cluster tool systems are not MESC-compatible. While there is a growing portion of MESC-compatible cluster tools, the standard does not make a significant impact on customers' buying decisions.

4.7.1.1.2 Development of Dry Stripping Equipment Industry

Photoresist removal is a surface cleaning process. Originally stripping was only a wet process, but today it is done primarily with plasma strippers. This is because wet chemistries have a difficult time completely removing resists with today's complex topographies. Plasma strippers are safer and more efficient. However, the major disadvantage to plasma stripping is it can not remove all of the metallic ions. Therefore, wet chemical cleans follow plasma stripping for this reason.

The volume production of MSI ICs in the late sixties is what first drove the need for plasma strippers. Tracerlab, a subsidiary of LFE offered the first commercial plasma stripping system, the LTA-600J. The system was a small low-temperature (100-105 °C)



Source: Applied Materials
2245-27

Presentation 4.7.1.1.1-16

Inside View of the Precision 5000 Etch

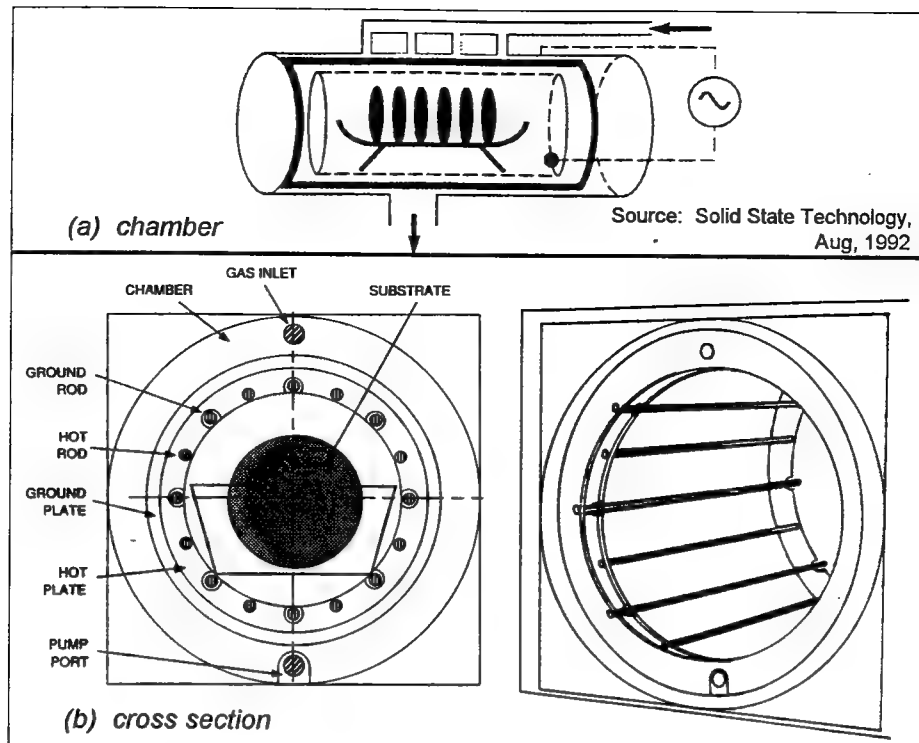
bench-top asher that sold for just over \$5,600. The typical gases used in this system were oxygen, hydrogen or helium.

In the early seventies, the basics of plasma stripping had become well established. Yet the process was not well understood, the qualification procedures were lacking and device degradation effects were unknown. The most common device problems encountered in MSI ICs was that the plasma strippers left inorganic residues on the wafer surface. This resulted in plasma stripping losing its appeal in MSI IC lines.

Another problem with stripping was the residues of tin impurities in the resist. At the time, this type of device degradation was not easily detected in a high production environment. As a result, it was not until the mid-1970s that plasma stripping could establish itself as a manufacturing mainstay in processing MSI ICs.

By the end of the seventies, most strippers came in barrel configuration and soon became known as barrel strippers. The Japanese still call them ashers. These systems are relatively cheap, effective and offer high throughput, but sometimes their wafer to wafer uniformity suffers. Early barrel systems caused radiation damage because these systems exposed the wafers to the RF energy source. However, today's newer barrel reactors lessen the radiation damage problem by using a Faraday cage around the wafers. Presentation 4.7.1.1.2-1 illustrates a barrel stripper.

In the eighties, the industry began to move away from batch barrel systems to planar downstream systems. Planar downstream systems improved uniformity. In addition, they further eliminated radiation problems by isolating the wafers from the RF field (see presentation 4.7.1.1.2-2). By the end of the eighties, such downstream systems made



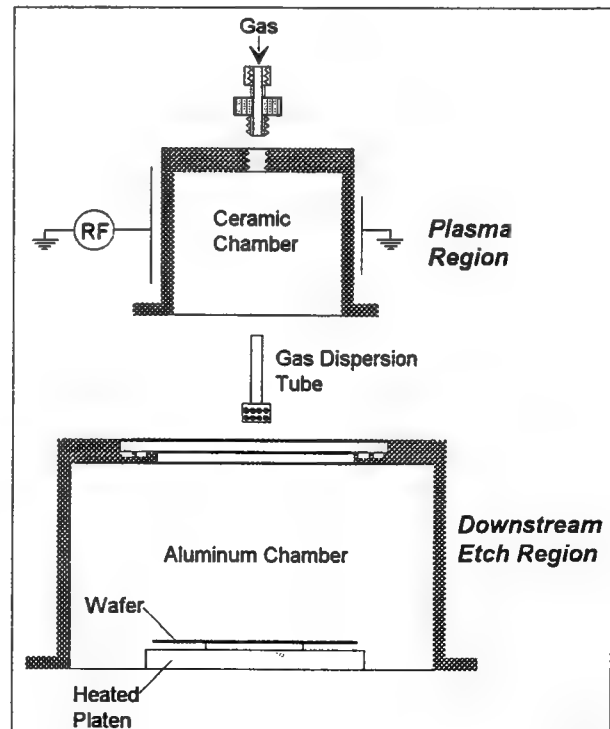
Presentation 4.7.1.1.2-1

Source: Technics
2245-29D

Barrel Photoresist Stripper

up about 50% of the overall photoresist stripping market. By this time, linewidth geometries had reached submicron levels. But downstream strippers used for these finer geometries, left behind too much residue. Therefore, alternative methods were tried for eliminating the residues. One was to increase the power level in barrel systems and blast the residue off. However, this increased device damage. As a result, the most common method to eliminate residue after strip was to continue to combine dry and wet stripping methods. A wet strip would follow the dry strip with an acid or a solvent.

Another dry stripping that was method developed was the UV photoresist stripper. Mitsui-Busan introduced the UV photoresist stripper in 1985. The system used a deep UV excited ozone (O_3) process. There were two main advantages to this system. The first advantage was the ability to strip ion implanted photoresists. These had always

Source: GaSonic
2245-30D

Presentation 4.7.1.1.2-2

Cross Section of a Downstream Photoresist Stripper Chamber

been tough to remove for the ions tended to overbake the resist. The second advantage was thought to be that there was no plasma to damage the devices. This was becoming more of a problem with VLSI geometries. However, UV photoresist strippers never caught on because the energy in the UV light source also tended to damage the wafers.

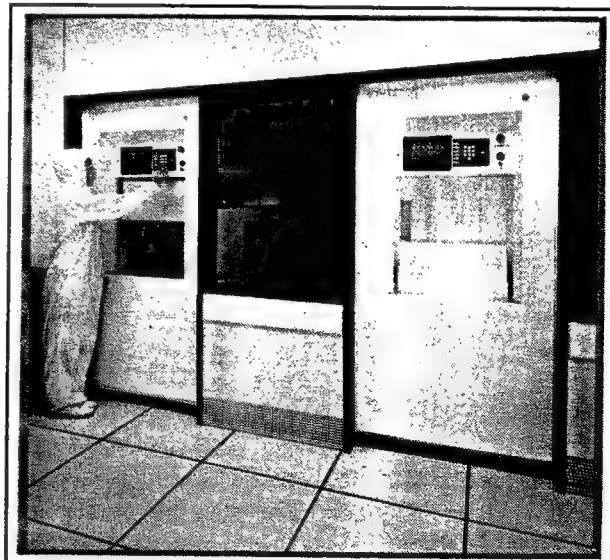
Fujitsu introduced an alternative stripping method that substituted a hydrogen plasma for the conventional oxygen plasma. The impetus for this system was Fujitsu's discovery that impurities exist in residuals of the oxide ash as well. The hydrogen plasma converted these oxides into stripable hydrides. Unfortunately, hydrogen plasma will also damage the substrate. Therefore, to get away from this, Fujitsu's system would strip the upper layer with hydrogen plasma and then use a conventional oxygen plasma to strip the lower layer. Fujitsu reported that this method reduced the amount of resist residue and reduced the likelihood of damage.

In 1990, Mattson Technology introduced the ASPEN, a parallel plate dry stripping system. This system was developed out of the need to eliminate damage and residue during the stripping process. High pressures are used in this system. The high pressure produces lower plasma potential which increases stripping rates. Advantages of the ASPEN are that residue, damage and particles are low, while throughput is high. In addition, wet cleaning steps are eliminated after stripping (see presentation 4.7.1.1.2-3).

4.7.1.1.3 Development of the Wet Processing Equipment Industry

Clean wafer surfaces are crucial to the reliable manufacture of semiconductors. Up until the late seventies, the focus upon

cleanliness was largely directed towards the clean room first and material purity second. Little attention was paid to the effect equipment and facilities might have upon the cleanliness of the wafer. Likewise, little attention was paid to other contaminant generators in the clean room. However, an exception was given to the specific contamination caused by people. It was assumed that most of the dirtiness was either generated by people from within or brought in from the outside. Attention towards cleanliness at the wafer surface itself was thus directed towards how to keep people away from the wafer surface. It was also focused on how to prepare a clean wafer surface once it had become contaminated. Because of this focus upon people, clean room garments became more and more complex. However, the wafer itself remained out in the open air, free to pick up anything that came along. This situation of protecting the worker from the wafer had evolved quite naturally from safety considerations. While worker safety is of foremost importance, protecting the wafer from the worker was not fully recognized until the late seventies.



Source: Mattson Technology
2245-56

Presentation 4.7.1.1.2-3

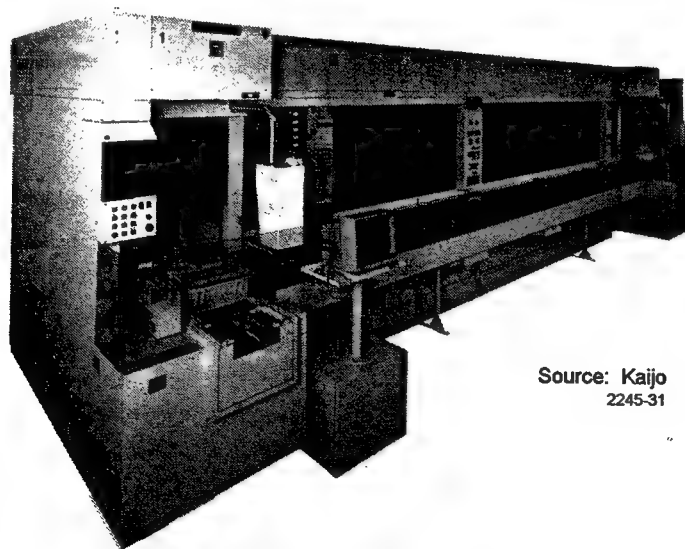
ASPEN Parallel Plate Dry Stripper

The roots of the concerns of cleanliness go back to a single event centered around mask cleaning that occurred in 1978. Two years earlier, in 1976, KLA had introduced the first automatic mask inspection system. Subsequently, at the Kodak Microelectronics Seminar, David Angel and P.H. Johnson of AMI astounded the lithography world with some of the first results from having used the inspection system. They had bought the system and set out to use it as a means for improving manufacturing via automation. What they found was an incredible number of defects not previously known to have existed. Angel and Johnson's results were soon repeated elsewhere. The semiconductor industry embarked upon a long and successful drive to implement automatic inspection. From this drive came equally astounding results elsewhere. First at IBM then at Hewlett-Packard, attempts were made to produce 'clean boxes' for storing clean wafers. They quickly found that the boxes themselves were flaking off dirt and were not clean. Equipment dirtiness then became the sharp focus and it was soon discovered that equipment was even dirtier than people. A drive to clean up equipment via automation followed. It was

then found that robots were dirtier still. At about the same time, Don Tolliver at Motorola began studies of liquids used in clean-rooms. He soon confirmed that liquids are also dirty. Therefore, by the late seventies, efforts began at all levels of manufacturing to improve the wafer environment and to develop a concept of 'wafer ecology'.

4.7.1.1.3.1 Development of the Wet Wafer Processing Equipment Industry

The earliest cleaning equipment was simple chemical apparatus available from conventional scientific distributors. It included sinks, boats, hoods, vessels, rinse tanks, etc. The only requirement was that it be lined with inert materials. Over the years, this miscellaneous collection of apparatus gradually took on the appearance of integrated work benches. Later, these work benches became known as workstations, wet decks, wet benches or dip & dunk stations (see presentation 4.7.1.1.3.1-1). They usually contained sinks for dipping and dunking wafers in etchants and D.I. water. The dip-



Source: Kaijo
2245-31

Presentation 4.7.1.1.3.1-1

Full-Auto Wetstation

|
VLSI RESEARCH INC

ping and dunking, or rather immersion method of cleaning the wafer is the oldest method used. Immersion baths are filtered, recirculating modules.

Rinsing and drying equipment evolved as a step upward from immersion bath cleaning. Rinser/dryers reduces particulate and metal ion contamination that is inherent in wafer processing. The equipment uses D.I. water to rinse and various methods to dry. There are two main methods used to dry the wafers. The first method dries the wafers by high speed rotational drying after the wafers are rinsed with D.I. water. The other method surrounds the wafers with isopropyl alcohol (IPA) vapor after the wafers are rinsed. The IPA vapor removes the rinse water. In some machines the wafers are purged with nitrogen gas to eliminate the IPA vapor.

Scrubbing was another wafer cleaning method that developed. Mechanical wafer surface scrubbers were developed in the sixties to improve wafer cleanliness requirements in epitaxial growth. The two types of scrubbers that were developed used either brushes or fluid jets. Scrubbers use mechanical forces to remove particles. They did not usually use active reagents.

Brush scrubbers use actual brushes, however, the brushes do not come in physical contact with the wafer. An intervening film of water exists between the wafer and the brush fibers. The brush scrubber technique was successful for removing particles greater than one micron and for removing tightly adhered particles. However, scrubbers gained the reputation of being a key source of contamination. The problem with brush scrubbers was the tendency to redeposit particles from the bristles.

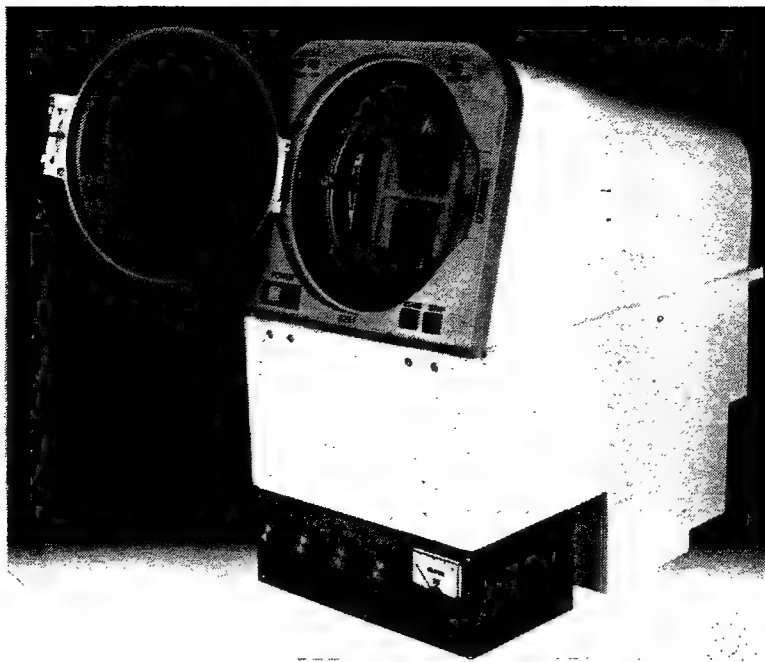
Fluid jet scrubbing was accomplished by sweeping a jet of fluid across the wafer. There were two advantages to fluid jet. One was there was no contact with hard

brushes. The second was the fluid could penetrate recesses too small to be affected by brush bristle size. However, the force required to dislodge particles approached the value of those which did product damage.

In the late seventies, FSI introduced the first centrifugal spray cleaning machine. FSI also pioneered the concept that chemical processing should occur within an enclosed chamber and that chemicals should be used once. This system rotated wafers past a stationary spray column. The wafers were then spun-dried in heated nitrogen. There were three advantages to centrifugal spray. One was that it reduced the volume of chemicals needed. The second was there was the continuous supply of fresh reagent solutions to the wafer surface. The third was that the environment was controlled during processing. Spray processors are also faster than are immersion techniques and can easily handle multiple solutions in the same chamber. Presentation 4.7.1.1.3.1-2 displays FSI's wafer spray cleaning system.

Plasma cleaning was also developed in the late seventies. It was used to remove organic photoresist from wafers. However, plasma clean did not become a predominant cleaning method. The method was effective enough to strip a photoresist, but it damaged the wafer substrate while leaving resist contamination. Plasma cleaners today are mostly used to etch the wafer surface to remove native oxides.

Most of today's cleaning techniques can be traced back to Werner Kern's work at RCA during the seventies. While at RCA, Kern invented the 'RCA standard clean'. The RCA clean is a two step process. The first step is called standard clean-1 or SC1. In SC1, the wafers are exposed to a hot mixture of hydrogen peroxide and ammonium hydroxide to remove organic particles by oxidative breakdown. The wafers are rinsed



Source: FSI
2245-34

Presentation 4.7.1.1.3.1-2

FSI's 8251 Clean System

and go on to the second step. The second step is called standard clean-2 or SC2. SC2 exposes the rinsed wafer to a hot mixture of hydrogen peroxide and hydrochloric acid. The RCA clean is the most common wafer cleaning method used today.

In the late seventies, Alfred Mayer at RCA developed the megasonic cleaning technique. This technique removes both contaminant films and particles in one operation. Similar to ultrasonic cleaning, megasonic uses piezoelectric transducers to generate sonic waves at frequencies of 850-900 KHz. The system uses a much higher frequency than does ultrasonic cleaning systems. Ultrasonic systems operate at 25 KHz.

The original megasonic patent rights were sold to four companies. Fluorocarbon, however, came out with the first production model that took advantage of the patent. It was a noncontact, brushless scrubbing ma-

chine designed to remove particulate contaminants from both sides of the wafer. Fluorocarbon found the fine particle cleaning system to be very effective. It was highly competitive with other conventional brush and high pressure water systems. In 1985, an investor and employee group purchased Fluorocarbon, the new company was named Verateq. Verateq continued to produce the megasonic cleaning system.

In 1987, CFM Technologies developed a closed chemical cleaning system termed Full-Flow (see presentation 4.7.1.1.3.1-3). In this system wafers are kept stationary within the system during the entire cleaning, rinsing and drying process. Because the wafers are totally enclosed in the system, and there are no moving parts, recontamination problems are minimized.

The late eighties saw another innovation: vapor phase cleaning. Vapor phase cleaning uses an anhydrous HF/vapor to clean native



Source: CFM
2245-36

Presentation 4.7.1.1.3.1-3

CFM's Full-Flow Wet Processing System

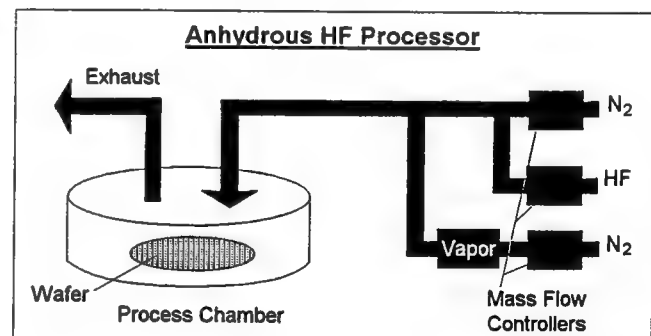
oxides from silicon and polysilicon surfaces at ambient conditions. However, this technology still requires a wet rinse, which is incorporated into the system. Vapor phase eliminates liquid chemical wastes and reduces the cleaning process steps. FSI's EXCALIBUR gas processing system was the first system to successfully use this tech-

nology. With the vapor phase concept, the wafer is placed on a pedestal inside the chamber. The chamber is sealed. A mixture of anhydrous HF and nitrogen gases are then injected into the process chamber through mass flow controllers (MFCs) (see presentation 4.7.1.1.3.1-4).

Advantage, (1988-1992) also introduced a vapor phase cleaning system. It was the Edge 2000, which used HF/H₂O and HCl/H₂O vapor phase technologies. However, the EDGE 2000 had a slow start. So, Advantage had to close its doors. In 1992, Genus bought the EDGE 2000 and its technology.

However, vapor phase technology has not been a strong contender against wet cleaning. Wet cleaning is still the best process for complete particle removal. Vapor-phase is used primarily to pre-clean tungsten silicides and polysilicon.

In the late eighties and early nineties, the impact of chemical waste upon the environment became a large issue. Both local and federal governments established environmental guidelines for reducing or eliminat-

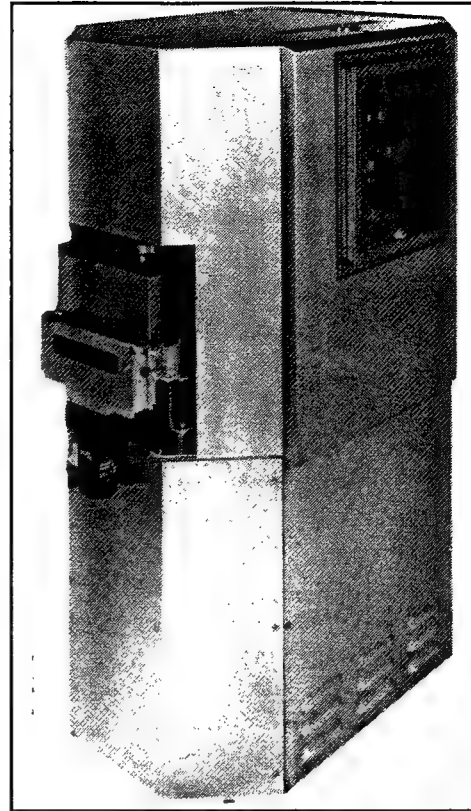


Source: FSI
2245-37D

Presentation 4.7.1.1.3.1-4

EXCALIBUR™ Vapor Phase Concept

ing the usage of chemicals and chemical waste. One such federal law was the Resource Conservation And Recovery Act. Another law was the Clean Air Act of 1990. This act called for the immediate reduction of CFC use as well as its complete phaseout by 1995. The act also mandated a law requiring a warning label on all products using CFCs in the manufacturing or cleaning process. Environmental concerns with chemical use in the semiconductor industry prompted research into ways of reducing, recycling and eliminating many chemicals. Wet processing equipment was examined very closely since it generated large amounts of chemical waste. As a result, cleaning equipment which used fewer chemicals began showing up on the market. One system was the SP200 cluster clean by Sub-Micron Systems, Inc. (see presentation 4.7.1.1.3.1-5). Another was the Plasma Chemical Cleaning Module (PC2M) by Balzers. Both systems use dry-cleaning methods. The SP200 uses a UV-excited gas technique to clean the wafers. The PC2M uses a low energy DC gas discharge in a argon or hydrogen atmosphere to remove contaminants.



Source: SubMicron Systems
2245-38

Presentation 4.7.1.1.3.1-5

Cluster Clean-SP200

4.7.1.2 Technology of Etching and Cleaning



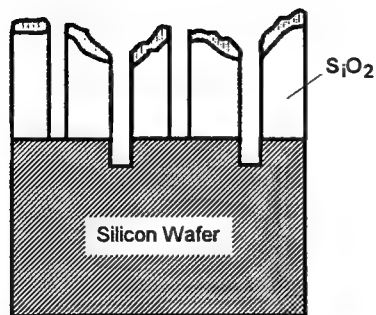
- Low pressure systems are key to etching sub-micron linewidths.
- Wet chemistries remain the most effective method for particle removal.
- Environmental concerns are influencing the need for alternative cleaning processes.

4.7.1.2.1 Dry Etching Technologies

Various etcher technologies are on the market today. The variety of circuits produced require different etcher technologies. These etchers basically fall under two categories: high pressure systems and low pressure systems. High pressure systems generally operate at or greater than 50 mTorr. They are used for production of devices that require greater than half micron geometries. Low pressure systems generally operate below 50 mTorr. They are used for the production of devices that require less than half micron geometries. The high pressure technologies consist of the conventional planar plasma systems, reactive ion etching (RIE), and magnetically enhanced reactive ion etching (MERIE). The low pressure technologies include electron cyclotron resonance (ECR), helicon wave, inductively or transformer coupled plasma, and high-density reflected electron (HRe).

The advanced circuits being produced today require uniform, anisotropic etch processes. They demand processes which incorporate increased numbers of mask layers, topographical variations and decreased dimensions. Therefore, the key driving forces for dry etching equipment are selectivity, uniformity and CD control.

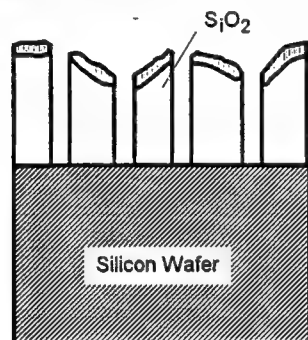
Selective etching is important for achieving uniform etch rate in non-uniform films. A uniform etch rate will result in equal etch depths across the entire film surface. This is true even when film thicknesses are non-uniform. However, if the etch is not selective but film thicknesses are non-uniform, a uniform etch rate will not result in over etch of the underlying film. This is because without selectivity the etcher will cut into the lower layers or into the substrate where the upper film is thin (see figure A of presentation 4.7.1.2.1-1). For example, suppose the upper film's thickest areas are 5000 Angstroms thick and the thinnest areas are 3500 Angstroms. Further, assume that the film can be etched at 1000 Angstroms per minute, while the selectivity is 10:1. The thin regions will etch in 3.5 minutes, while the thickest areas will require five minutes. During the extra 1.5 minutes, the underlying substrate will be etched 150 Angstroms while the remaining 1500 Angstroms of the film's thickest areas are etched. Therefore, high selectivity is needed to guarantee minimal etching of the underlying silicon (see figure B of presentation 4.7.1.2.1-1). A highly selective process will go right on etching in the unfinished areas while it comes to a virtual stand still in the finished areas.



Without Selectivity

Figure A

Uniform etch rate with poor selectivity often results in a non-uniform etch, and undercutting at the interface.



With Selectivity

Figure B

Uniform etch rate with high selectivity results in a uniform etch.

Source: VLSI RESEARCH INC
2245-13D

Presentation 4.7.1.2.1-1

Etching Non-Uniform Film Thicknesses

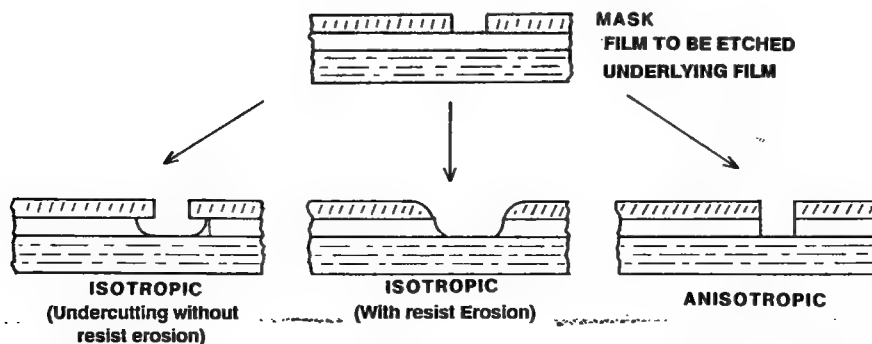
Critical dimension (CD) control is another important variable that must be controlled during etching. In fact, it was the inability to control CDs that hastened the demise of wet etching techniques. Wet etching is isotropic, that is it etches more or less equally in all directions. Isotropic etching methods etch feature sidewalls at the same rate. It also can erode the resist mask or etch the film under the mask thereby enlarging features (see presentation 4.7.1.2.1-2). Planar dry etching methods are usually anisotropic, that is they etch in one direction. Optimally this results in straight and vertical sidewalls. As a result, nearly all etching is done with dry techniques.

Planar Plasma Systems

Of the dry etching technologies used today, conventional planar plasma systems have been around the longest. In this etcher, two parallel electrode plates are located horizontally above each other in the etching chamber. A wafer is placed on one of the electrodes which is maintained at ground potential. RF power usually at 13.56 MHz, is applied to the opposite electrode. The pressure in the chamber is set between 0.1 to 0.01 Torr by the vacuum system and a reactive gas is admitted into the chamber. A plasma is then generated as the gas flows between the two parallel plates (see presentation 4.7.1.2.1-3). Administering high pres-

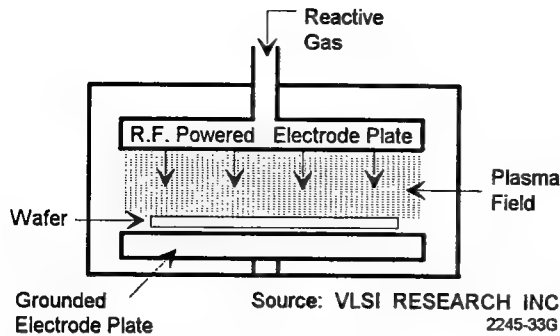
Presentation 4.7.1.2.1-2

Isotropic Versus Anisotropic



Source: VLSI Electronics, Vol. 8
2245-14

VLSI RESEARCH INC



Presentation 4.7.1.2.1-3

Schematic of a Planar Plasma Etch Process Chamber

sure and high power to the plasma confined between the plates results in high plasma density. This technology produces high etch rates and good anisotropic profiles. However, planar plasma systems are unable to accomplish satisfactory anisotropic profiles at geometries below 2 microns.

Reactive Ion Etching System

Reactive ion etching (RIE) systems pick up where planar plasma leave off, etching excellent anisotropic profiles below 2 micron design rule. RIE employs some planar plasma technology. It uses two parallel plates, and generates the plasma between the two plates. However, the pressure is reduced to between 0.1 and 0.001 Torr. In addition, the RF powered and the grounded electrodes are reversed, with the wafer now being placed on the powered electrode. RF power is capacitively coupled to the electrode, to block DC currents. The electrode is charged by interaction with the plasma. This charging takes place in the first few milli-seconds after applying the RF power.

This phenomenon can be visualized by studying the motion of the electrons and ions in the plasma near the electrodes surfaces. A plasma is a highly conducting ionized gas. It is made up of equal quanti-

ties of negatively and positively charged atoms as well as some neutral atomic gas. Most of the negatively charged atoms are electrons. These electrons have less mass than the heavier positively charged atoms. In a planar plasma etcher the electrode where the wafer sits is grounded. Therefore, when the plasma comes in contact with the grounded electrode, the overall potential of the plasma is zero. However, the situation is quite different near the RF powered electrode. During the positive half-cycle of applying RF voltage, electrons are attracted to the electrode and ions are repelled. Since electrons are much lighter than ions, they travel further and faster, eventually striking the electrode. Some of these electrons are captured by the electrode. During the negative half-cycle, the opposite occurs. However, in this case fewer ions collide with the electrode than did electrons in the previous half-cycle. Since no thermionic emission takes place from the electrode, it is left with a net negative charge. The electrode circuit is DC blocked, so no DC current can flow and the charging of the capacitor begins. This process continues through subsequent positive and negative half-cycles of applied RF voltage. The charging of the blocking capacitor continues until the total negative potential on the electrode is sufficient to attract as many heavier, positive ions as electrons. The net result is a potential difference between the plasma boundary (near ground potential) and the negatively self-biased electrode. A plasma sheath or dark space is created between the plasma boundary and the wafer's surface. A small uniform electric field perpendicular to the wafer surface is established in this sheath region. The sheath assists in the etch rate and direction of the etch. The ions and free radicals are accelerated toward the wafer's surface by the sheath field. Thus, material is removed from the wafer surface as a result of two actions. The first action is the chemical and physical reactions between the free radicals and the film material. The second action is

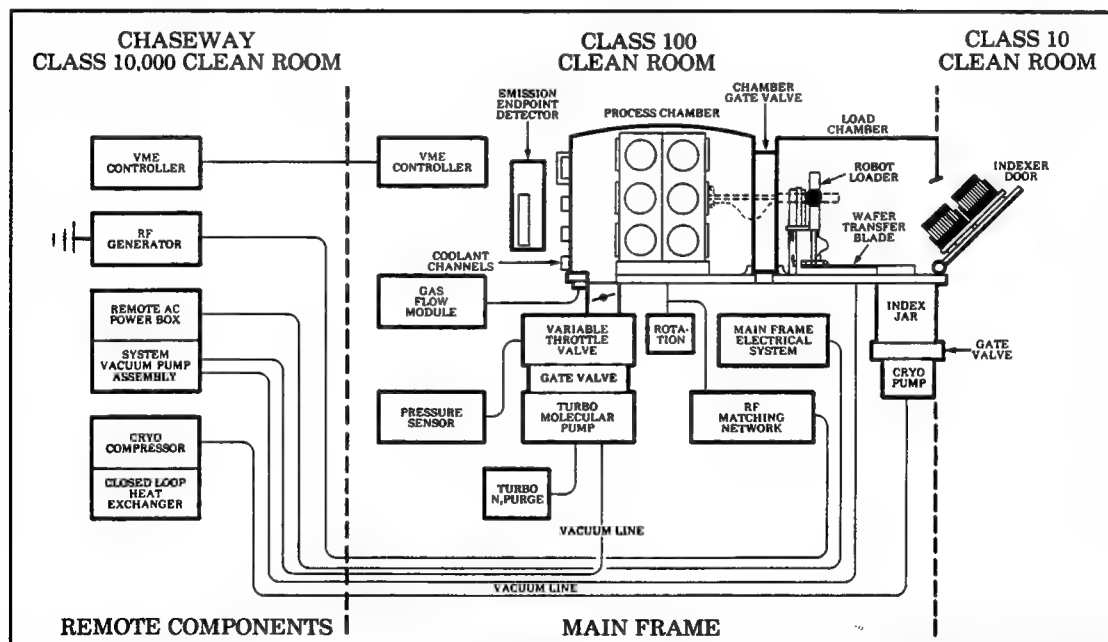
by the physical bombardment of ions. RIE is more effective than conventional plasma etching. This is because these energetic ions selectively remove nonreactive etch by-products that inhibit the etching process. The ion energy (sheath potential) of the process can be increased either by raising the RF power or by lowering the pressure in the chamber. The components of an RIE system can be found in presentation 4.7.1.2.1-4.

An RIE system has several disadvantages. One is it produces low etch rates. This is because it operates at reduced pressures. In response to the low etch rates, RIE etcher manufacturers use batch reactors. With batch reactors, many wafers can be etched simultaneously, thereby increasing throughput. A second disadvantage is that it is not as good for etching polysilicon on gate oxides. This is due to radiation damage to the oxide and a tendency for under

cutting. Another disadvantage is that physical damage to the surface can occur. This is due to the sheath potential's self-biasing effect which accelerates ions toward the film surface.

Magnetically Enhanced Reactive Ion Etching Systems

As a response to improve RIE, magnetically enhanced reactive ion etching (MERIE) was developed. MERIE uses the same basic technology as RIE systems, but the intensity of the plasma is increased by using a magnetic field. Electromagnets are used to produce the magnetic field. Use of electromagnets provides the ability to vary the magnetic flux as well as rotate the field. By varying the field strength and the rate of rotation, individual processes can be further enhanced to provide improved uniformity, etch rate and selectivity.



Source: Applied Materials
2245-39

Presentation 4.7.1.2.1-4

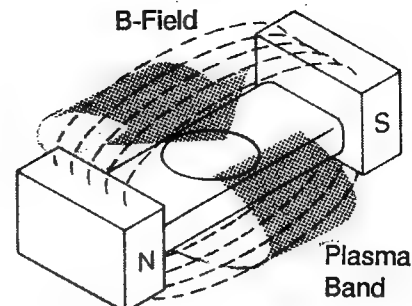
Schematic of an RIE System
(Precision Etch 8300)

The magnetic field is applied perpendicular to the electronic field and parallel to the wafer's surface (see presentation 4.7.1.2.1-5). The magnetic field merges with the plasma sheath potential, confining the electrons in the plasma thus preventing their escape. This increased electron density increases the collision probability between the electrons and the reacting gas molecules. It also reduces electron collisions with the electrode. This results in increased ion density within the plasma and more reactive atoms available for etching. This design also reduces the amount of self-biasing on the electrode. This means that the reactant ions have less energy to impinge upon the film surface. Therefore there is less film erosion while maintaining high etch rates through enhanced plasma density. The key advantages of a MERIE system are enhanced etch rates at low pressures and lower damage. In addition, MERIE allows the benefits of the RIE process in a single wafer reactor. Radiation damage is reduced by allowing lower sheath potentials and the magnetic field improves the ability to control the etch process without excessive heating. A schematic of a MERIE process chamber is shown in presentation 4.7.1.2.1-6.

Problems associated with MERIE systems occur primarily at the silicon level. Even though ion energies are lower, plasma densities are high enough to cause dopant depletion in silicon. Also, the high hydrogen content in the plasma injects hydrogen into the silicon and ties up dopants. This keeps the dopant from being activated and raises contact resistance.

Triode System

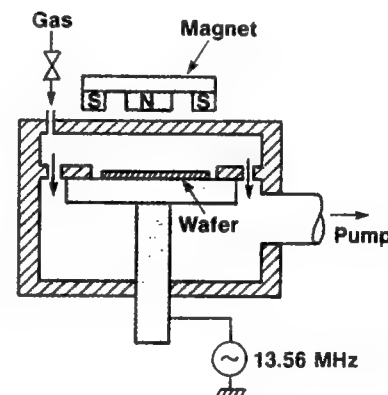
Triode systems were developed to capitalize on the strengths of conventional and RIE plasma systems. Conventional plasma has better etch rates and RIE systems provide better anisotropic etches. Triodes are essentially hybrids of a conventional and an



Source: MRC
2245-42

Presentation 4.7.1.2.1-5

Diagram of the Magnetic Field in a MERIE System



Source: Tylan/Tokuda
2245-41

Presentation 4.7.1.2.1-6

Schematic of a MERIE Process Chamber

RIE plasma system. It contains three planar plates. Triode systems' plates are configured in different ways. One configuration consists of the three plates being horizontally spaced, one above the other. Another configuration has two of the plates being horizontally spaced above each other with the third vertically positioned at the end of the other two. In both configurations, two plates are powered while the third remains

grounded. Depending on which plates are powered, a full downstream effect, a full RIE effect or a combination of the two effects can be accomplished. The ability to power any combination of electrodes provides substantial process flexibility. By controlling the ratio of the two power supplies, etch rates and anisotropy can be increased. In addition, the need for a high power input is lessened, therefore lessening wafer damage (see presentation 4.7.1.2.1-7).

Wafer etching for advanced technologies requiring linewidths below half micron range requires low pressure operation, high plasma densities, and plasma confinement. These requirements produce high etch rates, CD control and clean etching. At low pressures the etch rates are low, to increase etch rates, plasma enhancement is required. Some methods for plasma enhancement are electron cyclotron resonance, high-density reflected electron, inductively or transformer coupled plasma, and helicon wave.

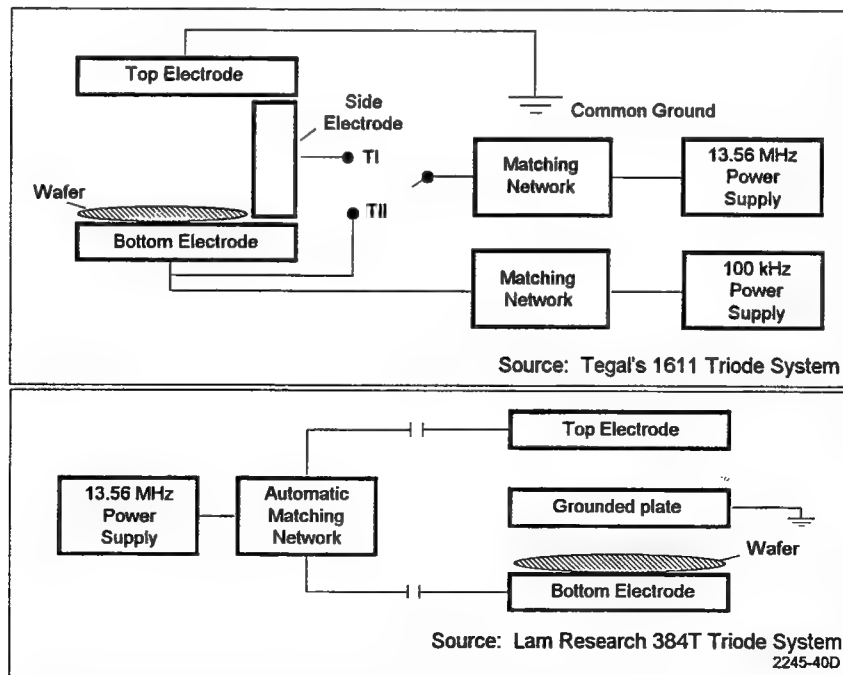
Electron Cyclotron Resonance

The name "electron cyclotron resonance" describes a charged electrons' reaction to microwave energy when all conditions are ideal. A charged particle in an electromagnetic field will undergo a constant change in direction. A resonance phenomenon will occur if the pressure, the electric field strength, the magnetic field strength and frequency of the applied electric field are properly matched. This resonance phenomenon results in a very intense plasma. The electrons in the plasma sheath are free to move in step with the applied voltage. At the resonant frequency, the electrons will circulate in a nearly closed orbital path. The resonant frequency lies in the microwave region of the electromagnetic spectrum. The frequency most often encountered for electron resonance is 2.45 GHz.

With ECR, a high density plasma is created in either a separate chamber or a remote

Presentation 4.7.1.2.1-7

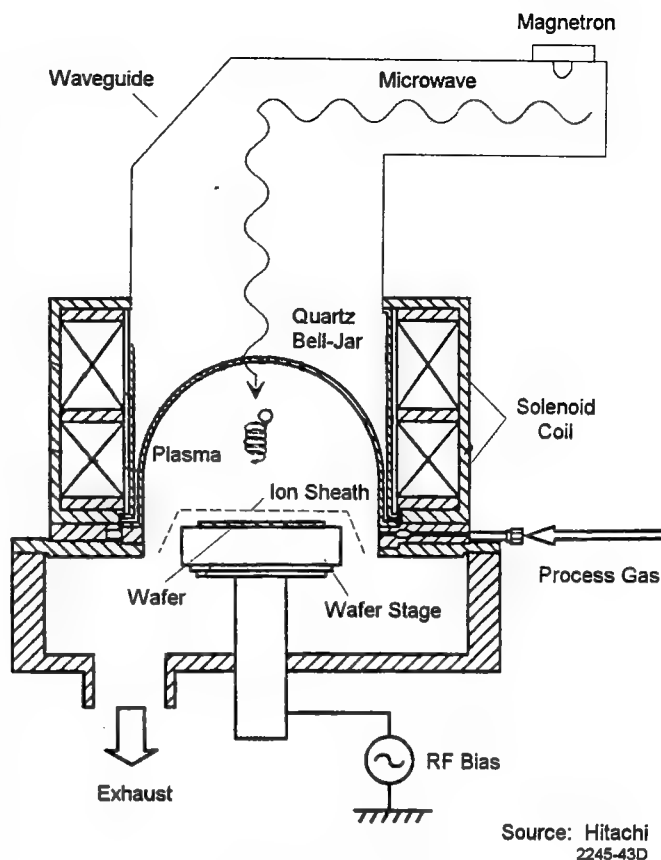
Two Configurations of a Triode Etch System



location within the chamber. The plasma is then diffused to the wafer area. Magnets are used to control the plasma density uniformity across the wafer. The basic idea in creating an ECR plasma is to couple microwave energy to the natural resonant frequency of an electron gas in the presence of a static magnetic field. The most common way to do this is by using a magnetic mirror or a streaming source design. Here, microwave energy is remotely generated and channeled down a waveguide, through a quartz window and into a reaction chamber. This chamber is filled with gas and surrounded by magnetic coils or solenoidal magnets. Inside the chamber, a very high density plasma is generated. The reactive ions stream downward to the wafer surface, or are directed to the wafer by a second set of magnetic coils. The etchant ions then drift out of the source aperture toward the wafer surface, diffusing and expanding as they follow the magnetic field lines to cover the entire wafer. Some systems make use of auxiliary magnets which are located behind the substrate container. The use of these auxiliary magnets allow the magnetic field to be shaped within the vicinity of the substrate. The auxiliary magnets also improve the uniformity control by forming a perpendicular magnetic field near the wafer (see presentation 4.7.1.2.1-8).

An ECR system can be operated in two modes of operation. One mode, used for isotropic etching, is similar to planar plasma etching in which the substrate holder is grounded and no self-bias is maintained. In this mode, the free radicals and ions diffuse outward from the source and impact the wafer with energies of less than 20 eV in a somewhat random direction.

The second mode of operation is used for anisotropic etching. Here, the wafer holder is powered with a low frequency, low RF power supply. This low frequency RF field creates a plasma sheath similar to that found in the RIE system. The ions are then



Presentation 4.7.1.2.1-8

Schematic of an ECR Chamber

accelerated across this self-bias and induce a small RIE effect. Typically only a small amount of RF power is used, usually under 100 Watts resulting in 10 to 50 volts of self-bias. This is sufficient to produce anisotropic profiles and to improve etch rates. These low bias potentials also result in improved selectivities compared to conventional RIE systems.

There have been many disadvantages associated with ECR. It is complex and costly. Wafer damage is more frequent because of the magnetic fields. It is difficult to produce a plasma with a large diameter and uniform etch rate across the wafer in the magnetic field. Finally, there have been microloading problems with 200 MM wafers.

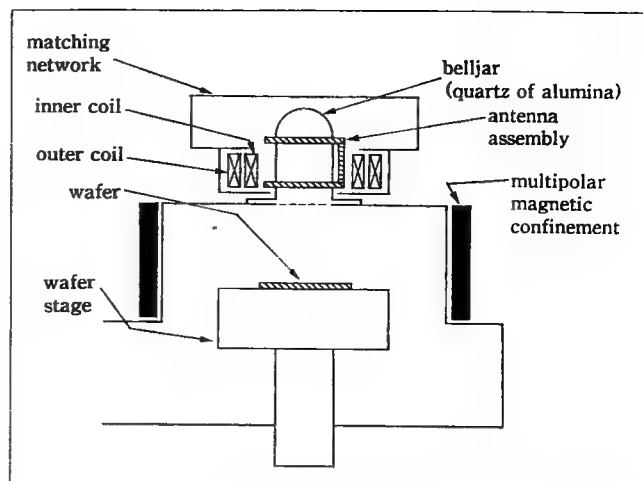
Helicon Wave

Helicon wave etch systems also generate the plasma in a source area away from the wafer. In the source area, an antenna wrapped around a quartz tube is powered at 13.56 MHz. An inductively coupled wave goes through the quartz tube creating an electro-magnetic field which controls the uniformity of the plasma. The plasma is then diffused to the wafer. The pressure inside the chamber is between 1 mTorr and 5 mTorr. The magnetic field is weak outside the source area, and is zero at the wafer level. So no unnecessary stress is placed on the wafer. The wafer can be biased if desired. Magnets are placed in the chamber wall. They form a bucket like field to capture and control the direction of the plasma (see presentation 4.7.1.2.1-9).

Inductively Coupled Plasma

Inductively coupled high density plasma technology makes use of a low pressure (5 mTorr) high ion density plasma source. This technology uses two parallel plates inside the etch chamber. The plasma is generated between the plates by an inductive coil powered at 2.0 MHz RF. The inductive coil is attached vertically to both sides of the chamber wall. The resulting high density plasma is generated above the wafer in a planar manner and is shaped uniformly across the diameter of the chamber. This produces a uniform etch across the wafer surface. The wafer is biased by a 1.8 MHz signal to control the energy of the ions extracted from the plasma (see presentation 4.7.1.2.1-10).

Lam Research's transformer coupled plasma (TCP) technology is similar to an inductively coupled plasma. However, the placement of the coil, the amount of power and the vacuum pressure is different. The coil is placed horizontally above the wafer and is powered by a 13.56 MHz RF to create and shape the plasma discharge. The pressure



Source: Semiconductor World, 1993.8, P.72
2245-46D

Presentation 4.7.1.2.1-9

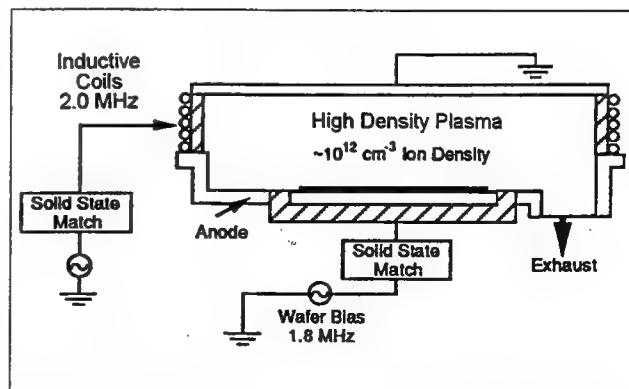
Helicon Wave Plasma Chamber

in the chamber is between 1.5 mTorr and 5 mTorr. In addition the wafer is biased by the 13.56 MHz power supply.

Magnets are not used with either systems, therefore wafer damage associated with these magnets is not a problem. Other advantages to these two technologies are better CD control, no radiation damage, minimal microloading and low foreign matter and particle contamination.

Presentation 4.7.1.2.1-10

Inductively Coupled High Density Plasma Chamber



Source: Applied Materials
2245-45

High-Density Reflected Electron

Tegal Corporation introduced the high-density reflected electron (HRe) technology. HRe etch technology was formerly called magnetically confined reactor (MCR). However, MCR was often confused with MERIE. So, Tegal changed the name to high-density reflected electron. HRe technology incorporates three electrode plates from Tegal's triode system. Two of the plates are horizontal while one is vertical. The vertical electrode is powered by a 13.56 MHz power supply to control ion flux. Less than 500 KHz is applied to the lower electrode to provide wafer bias and control ion energy. The upper electrode is grounded. The pressure is less than 5 mTorr. This technology uses a magnetic field to contain the plasma. Permanent magnets are bolted around the outside of the etch chamber. This creates a magnetic field container inside the chamber and is limited to the wall area of the reactor. The magnetic field acts like a physical barrier from the etch chamber wall, much like a container inside of a container. At the wafer, the field is uniform and weak. To create a high-density plasma at low pressure, a high ionization efficiency is required. HRe achieves this by increasing the path length of electrons travelling through the plasma. Electrons travelling toward the magnetic field wall are reflected by the magnetic fields back into the plasma (see presentation 4.7.1.2.1-11). The HRe design is simple and has low consumable costs.

4.7.1.2.2 Ion Milling Technologies

Ion milling is another dry etching technology. It is discussed separately from the other etching methods because it is strictly a physical process. Consequently, it can etch any material, but it has virtually no selectivity. In an ion milling process, the wafers are placed in a vacuum chamber and the pres-

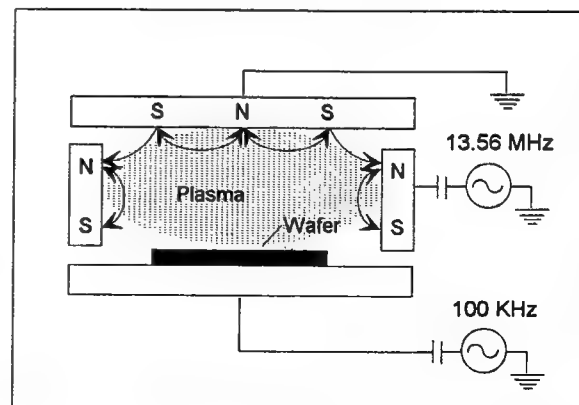
sure is reduced to 10^{-4} to 10^{-5} Torr. A high efficiency, multiple aperture ion source is used to produce an intense, collimated beam of Argon ions. These ions are focused and directed toward the surface of the film being etched. Upon impact with the film's surface, the surface is physically eroded in a momentum transfer process. The chamber of a typical ion mill is illustrated in presentation 4.7.1.2.2-1.

Ion milling processes can be either passive or reactive. Passive ion milling provides complementary processing capabilities where conventional plasma and reactive ion etching processes are limited. Reactive ion milling is similar to reactive ion etching. It provides some degree of chemical selectivity and end point detection which is not available in conventional ion milling. High energy ion milling can erode conventional resist materials at rates equivalent to the etch rate of the substrate film material being etched.

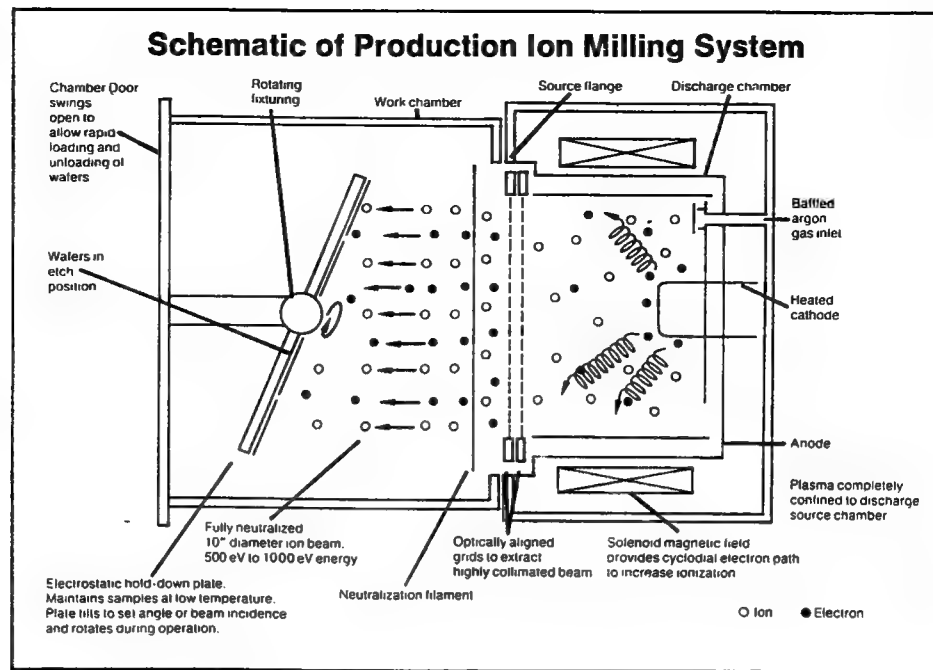
The advantages of ion milling are high resolution, anisotropy and residue free etching. The material removal is highly directional, which results in good definition of small openings. This process allows direct control over the angle of incidence

Presentation 4.7.1.2.1-11

HRe Process Chamber



Source: Nikkei Sango Shimbun
2245-47D



Presentation 4.7.1.2.2-1

Source: Veeco
2245-49

Schematic of an Ion Milling Process Chamber (Microetch)

with which the ions strike the surface. The disadvantages include the lack of selectivity, low etch rates, trenching redeposition and damage. Damage can occur from the ionization mechanism even though wafers are physically isolated from the plasma.

more uniform, more repeatable and it improves cost effectiveness over wet methods.

There are three types of dry stripping technologies currently used. They are barrel, downstream and parallel plate photoresist stripping.

4.7.1.2.3 Dry Stripping Technologies

The last dry processing procedure to be described involves photoresist removal. Resist removal results when atomic oxygen reduces the resist polymer chains to simpler groups. The oxygen plasma employed does not attack underlying surfaces nor does it introduce contamination. Dry photoresist stripping methods have replaced wet stripping methods on most manufacturing lines. This is because dry stripping offers more advantages over wet stripping. Dry stripping is a one-step process with a controlled reaction. It provides operator safety. It is

Barrel Strippers

Barrel strippers are the oldest dry stripping systems used today. Barrel strippers are batch quartz cylindrical systems which operate in the pressure range of 0.5 to 1.0 Torr. The wafers are stacked vertically within a self-shielding electrode tunnel (Faraday cage) to minimize ion radiation by the charged plasma. The quartz barrel is heated externally from radiative heaters or lamps by a 13.56 MHz power supply. This type of heating controls stripping rates and reinforces production throughout every cycle.

Disadvantages with barrel strippers are poor uniformity, limited 200 mm wafer capability, difficult to automate, some radiation damage and incomplete resist/residue removal. In addition, even though the barrel temperature can be controlled, the plasma temperature can not be.

Downstream Strippers

Downstream strippers are single wafer systems. Single wafer systems are preferred because they have better process control. In a downstream reactor the plasma generation and stripping take place in two physically separated areas. These two areas are connected together by a quartz or fluorocarbon lined tube or channel. The plasma is generated by subjecting oxygen gas to a high intensity ultraviolet or radiation source. The plasma then migrates downstream from the source chamber into the stripping chamber to the wafer. Once there, the plasma proceeds to attack and strip the resist from the wafer. The stripping chamber is outside of the high energy field. Therefore, higher energy can be imparted to the reacting species without subjecting the wafer to the energy source (see presentation 4.7.1.2.3-1). Two disadvantages with downstream strippers are residue remains after stripping and throughput is low.

Since linewidth geometries have reached submicron levels, both barrel and downstream strippers can not remove all metallic ions which exist in most resists or that have been acquired in prior wafer processing activity. To eliminate these ions, wet chemical cleans have to follow these plasma stripping methods, particularly

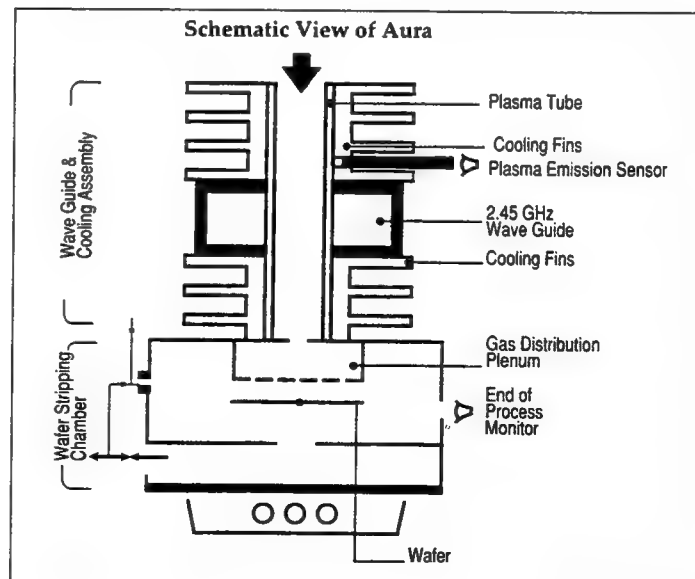
when high temperature furnace operations follow. Better results are obtained when a combined dry-wet process is used.

Parallel Plate Strippers

Mattson Technology developed the parallel plate stripper in order to eliminate the wet clean process after dry stripping. With it, only a DI water rinse is needed after stripping. Parallel plate stripping systems are similar to etching parallel plate reactors with adaptations for stripping. Mattson Technology came out with a diode and triode configuration (see presentation 4.7.1.2.3-2). In parallel plate strippers, wafers are placed on resistively heated support electrodes at 13.56 MHz. The plasma is created between the parallel plates. Pressures are relatively high (greater than 10 torr). High pressure produces moderately lower plasma potential and increases stripping rates. The advantages of parallel plate strippers are the residue, damage and particles are low and throughput is high.

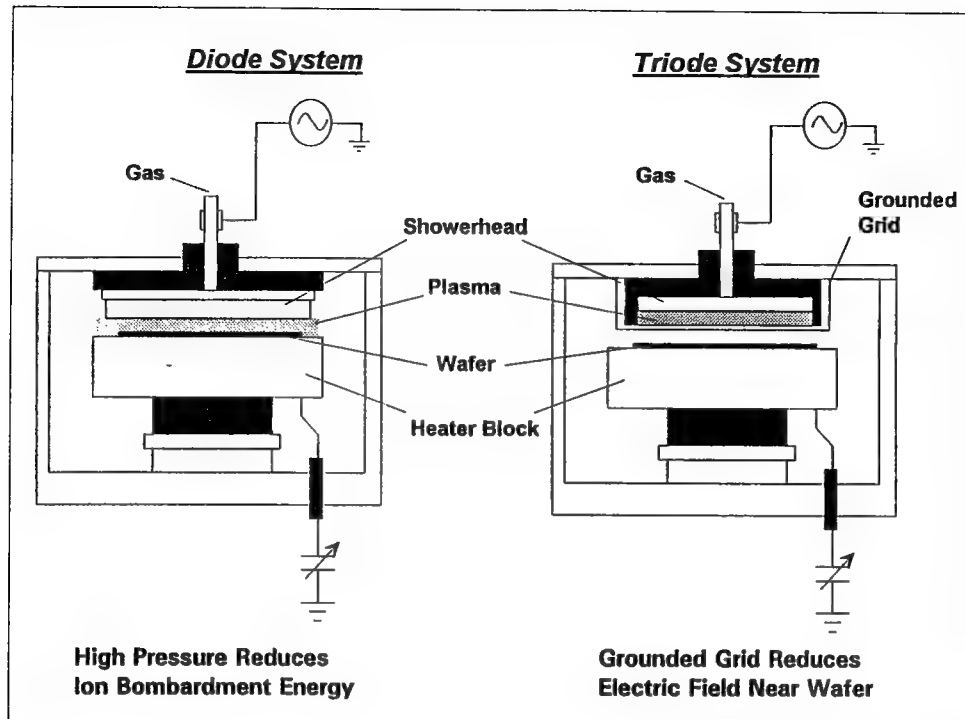
Presentation 4.7.1.2.3-1

Schematic View of the Aura Photoresist Stripper



Source: GaSonic
2245-48

Aspen Parallel Plate Dry Stripper Configuration



Source: Mattson Technology
2245-57

4.7.1.2.4 Wet Wafer Processing Technologies

Now that the critical dimension of devices has been reduced to submicron levels, the cleanliness of the wafer's surface has become more important in the manufacturing process. The increased importance of removing even the smallest contaminants has placed renewed emphasis on the whole wet process. Particulate surface contamination is directly responsible for low yields in the industry. Therefore, the industry is driven to improve cleaning techniques and performance to remove particle contamination.

Cleaning technologies concern those systems which are used to remove contaminants before they have had a chance to interact with the surface and create a defect. By-

and-large, this means removing the contaminant at the point of interaction—on the surface of the wafer.

Contaminants can come from many sources, but are generally derived from five key sources:

- Air-borne particulates
- Liquid-borne impurities and particulates
- Human 'dust'
- Manufacturing processes, facilities and equipment
- Materials impurities

Each of these sources contribute uniquely to the contamination problem and all must be removed. The difficulty in removing the contaminant are the adhesive forces that exist between the surface of the wafer and

the contaminant. Sometimes, as in the case of small particles, this adhesive force can be surprisingly strong.

There are two categories of phenomena that set in. The first is a physical phenomena that occurs when the contaminant first attaches itself to the surface. The second is adsorption which begins to take place almost immediately at the point of contact. Thus, time and temperature begins to take its toll. Eventually, some portion of the particulate is adsorbed through chemisorption. Once that begins, the process is irreversible and the contaminant can no longer be removed in its entirety through cleaning. Some form of mild surface etch must be used. This is why it is so important to remove contaminants quickly.

Turning first to the physical phenomena, there are four primary physical forces of adhesion that bind particles to a surface. They are capillary, van der Waals, electrostatic image and electrical double-layer. Capillary action can result in a strong adhesive force. Condensation of water vapor or other process liquids collect in the gaps between the particle and the wafer surface, thus forming a meniscus. The surface tension of this meniscus draws the surfaces together, resulting in capillary attraction.

There are several van der Waals forces. The one of greatest concern in semiconductor manufacturing is the so called van der Waals-London force, attributed to both van der Waals and London. The van der Waals-London attraction is an intermolecular adhesive force. Atoms that compose a particle are instantaneous dipoles. The dispersive interaction between these dipoles as well as the dipoles induced in neighboring atoms produces the attractive force.

Detailed studies of the van der Waals-London forces, concluded that van der Waals-London attraction decreases with the first power of the particle diameter. But

the mechanical stress necessary to remove particles decreases with the one-third power of a particle's diameter. Thus, the smaller the particle, the greater the difficulty in overcoming the van der Waals-London force. The entire cleaning process also becomes more difficult as a result.

Electrostatic image forces apply to particles larger than 5-micron. In conductors, this type of charge is neutralized by contact charge flow and thus electrostatic attraction becomes of minimal interest. In non-conductors, however, electrostatic attraction can be significant.

Electrical double-layer force is associated with particles below 5-micron. A surface contact potential is created between two different materials based upon each material's respective local energy state. The resulting surface charge buildup needed to preserve charge continuity set up a double-layer charge region, which creates the electrostatic attraction.

Some orders of magnitude are helpful here. In an air environment, the attractive forces between a one micron glass particle and a wafer surface are as follows:

Capillary	0.045 dynes
Van der Waals-London	0.014 dynes
Electrostatic Image	0.001 dynes
Electrical Double-Layer	0.003 dynes.

In contrast, the gravitational force on such particles is four orders of magnitude less than is the electrostatic image force. To better envision these forces relative to gravitation, consider the following comparisons:

Particle Size (micron)	Relative Adhesion Force in Air (g's)
500	2
50	200
5	20,000
0.5	2,000,000

Graphical data depicting these forces is given in presentation 4.7.1.2.4-1.

A common misconception about cleaning is that solubility of the particulate, per se, is a determining criterion for a good cleaning solvent. While high solubility is important, it is not particularly helpful for insoluble materials such as heavy metals. Rather, a good solvent will cause the disappearance of the capillary forces through total immersion and will thereby counteract this major force of attraction. A good solvent also provides charge neutralization, thus also reducing electrostatic forces. Nevertheless, even with these mitigating factors, the remaining physical forces of adhesion can still far exceed the forces that can be applied to remove the particle.

Bhattacharya and Mittal have shown that the force of removal is a function of the angle of the applied force. This can be seen with aid of presentation 4.7.1.2.4-2.

Here F_a is the force needed to remove the particulate, F_{ad} is the force of adhesion, and θ is the angle of the applied force. As can be seen, forces tangential to the wafer will be the most effective, forces normal to the surface will be the least effective. At equilibrium, the force necessary to shear off the particle is thus:

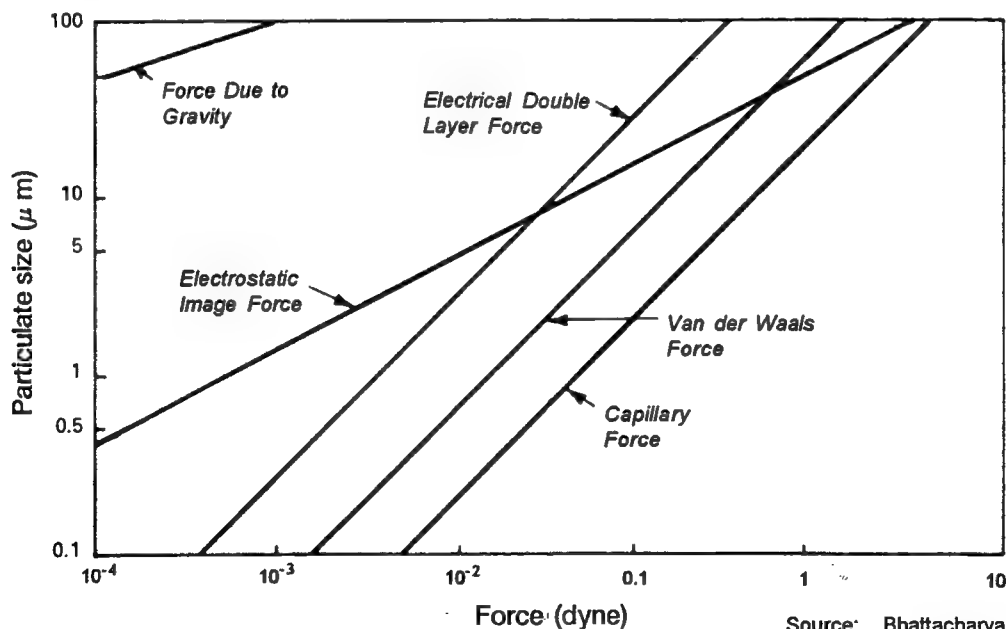
$$F_a = \frac{k F_{ad}}{\cos\theta - k\sin\theta}$$

Where k is the static coefficient of friction.

The magnitude of these forces of adhesion are as follows:

Capillary: $\pi\gamma d$

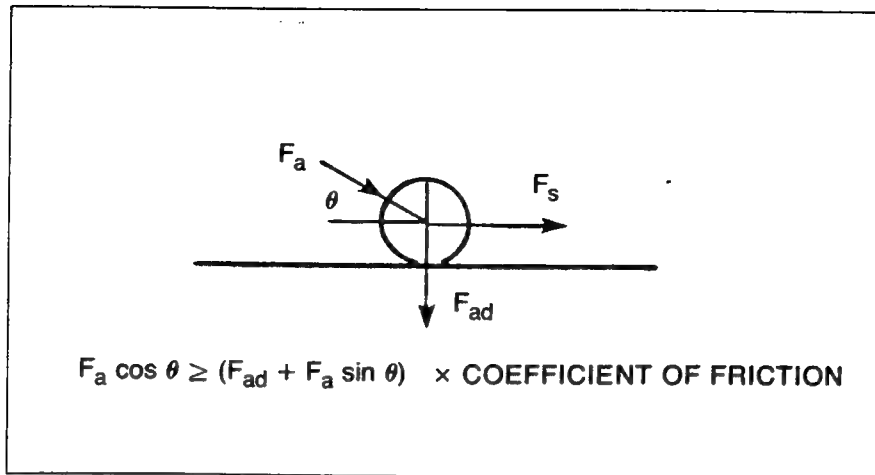
Electrostatic image force: $\frac{Q^2}{\epsilon d^2}$



Source: Bhattacharya
2245-60

Presentation 4.7.1.2.4-1

Summary of Adhesion Forces



Source: VLSI RESEARCH INC
2245-121

Presentation 4.7.1.2.4-2

The Action of Combined Forces on a Particle

Electrical double force layers:

$$\frac{\pi \epsilon_0 (\Delta \phi)^2 d}{2z}$$

Van der Waals force:

$$\frac{\hbar \omega d}{16 \pi d^2}$$

The variables and constants in these formulas are:

d = Effective particulate diameter, in cm.

z = Effective separation of particulate from the surface, $\approx 4 \text{ \AA}$.

γ = Water surface tension ≈ 73 dyne per cm.

$\Delta \phi$ = Workfunction difference $\approx 1\text{V}$

$\hbar \omega$ = van der Waals' constant $\approx 7.2 \text{ eV}$

ϵ = Relative dielectric constant

ϵ_0 = Permittivity of free space = 8.9 pF/m .

These equations hold for physical phenomena. However as mentioned earlier, adsorption also takes place at the point of contact. Adsorption is the adhesion of extremely thin layers of molecules of a gas, liquid, or dissolved substance or of particles to the surface of a solid substance. Adsorption takes place at the surface, resulting in an accumulation of increased concentration of molecules from the particulate in the immediate vicinity of the surface. As a familiar example—if freshly heated charcoal is placed in an enclosure with ordinary air, a condensation of certain gases occurs upon it; or if it is placed in a solution of unrefined sugar, some of the impurities are likewise adsorbed, and thus removed from the solution. Charcoal, when activated (i.e., freed from adsorbed matter by heating), is especially effective in adsorption, probably because of the great surface area presented by its porous structure. Its use in gas masks is dependent upon this fact.

At a given fixed temperature, there is a definite relation between the number of molecules adsorbed upon a surface and the pressure or the concentration.

The Freundlich or classical, adsorption isotherm is of the form:

$$\frac{x}{m} = kp^{1/n}$$

In which x is the mass of gas adsorbed, m is the mass of adsorbent, p is the gas pressure, and k and n are constants for the temperature and system. In certain system, it is necessary to express this relationship as:

$$\frac{x}{m} = K(h\gamma)^{1/n}$$

Where h is the relationship of the partial pressure of the vapor to its saturation value, and γ is the surface tension. Numerous isotherm equations have been proposed in the chemical literature in the last fifty years. The Langmuir adsorption isotherm is of the form:

$$\frac{x}{m} = \frac{k_1 k_2 p}{1 + k_1 p}$$

Such adsorption may be classified as either chemical adsorption (or chemisorption) where forces of chemical or valence nature between adsorbate and adsorbent are involved; or as van der Waals adsorption, involving chiefly van der Waals forces. Adsorption of the van der Waals type is exhibited by all substances, particularly at low and moderately low temperatures; it is chiefly characterized by relatively low heats of adsorption, namely about 5 to 10 kilocalories per mole of gas. These heat changes are of the same order as heats of vaporization; it appears, therefore, that the forces by which the adsorbed gas molecules are held to the surface of the solid are similar to the

forces of cohesion of molecules in the liquid state. In other words, the molecules are adsorbed by van der Waals forces, it is for this reason that the term van der Waals adsorption is used.

Another characteristic of van der Waals, or physical, adsorption is that for a given adsorbent the extent of adsorption, under constant conditions, is roughly related to the ease of liquification. There is a distinct parallelism between the extent of adsorption of a gas and its boiling point; the most easily liquefiable contaminants, that is—those with the largest van der Waals forces of cohesion—are those which are most strongly adsorbed.

The second type of adsorption is referred to as activated adsorption or chemisorption; the heats of adsorption are much higher than for van der Waals adsorption, the values being 10 to 100 kilocalories per mole. Chemisorption occurs in limited cases only, and it is generally observed at moderately high temperatures. Chemisorption is usually irreversible. As the temperature is raised the van der Waals adsorption, for an appropriate gas and solid, may pass over into chemisorption. As the name implies, chemisorption involves forces of interaction between the adsorbent and the gas that are chemical in nature, as distinct from the physical forces responsible for van der Waals adsorption. This accounts for the larger heat changes associated with the former type of adsorption.

Chemisorption—or activated adsorption—is highly specific in character, depending on the chemical properties of the contaminant and the adsorbent. Consequently, many gas-solid systems do not exhibit chemisorption at any temperature. The adsorption of oxygen or of carbon monoxide on tungsten is chemical in nature, as is evident from the fact that an oxide or carbonyl, respectively, of tungsten can be distilled from the sur-

face. Similarly, when oxygen is chemisorbed carbon monoxide and dioxide are obtained. Chemisorption also occurs with hydrogen and carbon monoxide. It is probable that in the chemisorption of hydrogen the molecules are either partly, or completely, dissociated into hydrogen atoms which are then held to the surface atoms by electron sharing.

These adhesive dynamics must be overcome by the cleaning equipment at nearly every step of the manufacturing process. The equipment used for cleaning by applying a physical force or by the application of a brief etch or polish.

Some generic groupings of the operations which require cleaning are:

- Microlithography, Etch and Implant
 - removal of unpolymerized resist
 - removal of polymerized resist
- Deposition
 - pre-deposition particulate removal (removal of possible ionic contaminants if high temperatures are involved)
 - pre-deposition film removal
 - post-deposition residue and film removal
- All processes
 - provision for inadvertent particulate, film and ionic contamination.

The need for the removal of photoresist after it has served its masking function is apparent. If the photoresist is not completely removed, the integrity of the next film is in jeopardy.

Predeposition, and any cleans for particles, is less straight forward. Particles may be organic or inorganic; they may be caused by people, equipment, indirect materials, or by the product itself. The bulk of these particles are organic. The inorganics include

metallic, quartz, silicon, particles and other 'debris'.

The selection of cleaning materials and methods for such a spectrum of contaminants is at best a compromise. Semiconductor product lines usually adopt one 'standard chemistry' for organics and another 'standard chemistry' for inorganics. Once chosen, the cleans are usually employed throughout the line, with little modification.

Predeposition film removal is much less complex. Films and their sources are easily identifiable. Certain oxide films in semiconductor manufacturing is expected. These are residual oxides from prior operations, or oxides acquired on silicon surfaces as a natural growth when exposed to ambient atmosphere, to water, or to prior cleaning reagents. Post operation films as well, usually consist of oxides grown in the course of the operation. These are known, so cleaning chemistry can be specific and efficient.

Other particulate debris accrued during the process step poses a severe challenge. These particles are principally silicon, quartz and redeposits of the deposition material itself. Here, the particles have the same composition as does the wafer. Chemical cleaning must then be augmented by mechanical removal. Process engineers attempt to avoid mechanical cleans due to concerns with product damage. A large portion of process engineering effort is devoted to prevention. Nevertheless, some product-lines do employ mechanically-assisted cleans as an interim measure.

Inadvertent contamination from a multitude of sources can occur in the course of processing. Sources include dropping a lot box, incorrect execution of the process (wrong materials or sequence), contamination of materials (process piping leaks), and particulate or film accumulation as a result of extended storage. With few exceptions, the

process engineer must determine if the contamination can be practically removed and what methods are to be used.

For physical removal, an air jet may be used to shear or roll the particle off the surface. For dry, uncharged particles, only the van der Waals–London and the electrical double-layer forces are present. It has been shown that air or nitrogen blow-off guns are effective in removing particles larger than 10 microns from surfaces but are ineffective in removing particles ranging from 1 to 10 micron in size. Recent experiments have also shown that air-jet effectiveness can be extended to half micron particles by taking into account the rolling action of the particle from the surface. However, the experiments also demonstrated that particles below 0.5 micron cannot be blown off.

The use of a liquid as the surrounding medium, rather than air or vacuum, helps reduce adhesive forces. Liquid cleaning methods, which employ spraying or agitation, tend to lower the van der Waals–London forces and to generate double-layer electrostatic repulsion forces that further facilitate particle removal. In fluid dynamic studies, force transfer to a particle that is separated from a surface by a liquid film has been shown to increase if the viscosity of the liquid is lowered. For example, different types of Freon and acetone have been proven to be highly effective in removing particles at relatively low accelerations (However, environmental concerns have limited the use of Freon). The relative success of acetone, and other organic cleaners compared with water has been attributed to the lower surface tension of organic cleaners.

Particles bound with capillary adhesion are difficult to remove despite the use of such liquids. Capillary adhesion, which binds particles deposited from a liquid suspension, is virtually impossible to overcome by chemical means. Even baking such liquid-depos-

ited particles at 180°C (a temperature greater than the liquid's boiling point) does not facilitate removal with an air jet. Subsequent attempts with ultrasonic and megasonic methods are not successful either. According to Bhattacharya and Mittal, the only means of removing these particles is to use through mechanical scrubbing. The implication for semiconductor manufacturers is clear: if the chemical cleaning fluid used reposit particles, then mechanical means will be necessary to clean the wafer.

To solve adsorption problems, it is usually necessary to use chemicals to mildly etch the surface. There are several wet chemical cleans such as this. The solutions used may be a variety of acids or bases, either organic and inorganic. Cleaning takes place by the oxidation and/or dissolution of contaminants. Wet chemical cleaning is useful for many types of particulate contamination and is essential for contaminants chemically bonded to the wafer surface.

While variation occur, a high degree of commonality exists in the industry's choices of wet chemicals. Presentation 4.7.1.2.4-3 provides a summary of some of these common chemicals.

One of the primary and most effective wet cleaning methodologies used today is known as 'RCA clean'. This method was developed by RCA engineers in the late sixties. RCA clean has become known as the terminology for any clean that uses hydrogen peroxide along with some other base or acid. The RCA clean is basically a two step process. First, the wafers are immersed in a water, hydrogen peroxide and ammonium hydroxide solution for 10 to 15 minutes. The bath temperature varies between 70 degrees and 90 degrees C. This bath removes organic contaminants. In the second step, the wafers are placed in a solution of water, hydrogen peroxide and hydrochloric acid. The time and temperature of the

Common Wafer Cleaning Chemicals

Acetone	Removes organic resists.
Ammonium Hydroxide (NH_4OH)	Relieves the hydrophobic nature of films so the acid solutions can penetrate.
Ammonium Persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$)	Removes resists and other organic materials.
Chromic Acid (H_2CrO_4)	Removes resists and other organic materials.
Di Water (H_2O)	Removes water soluble contaminants chemicals and loose materials.
Hydrochloric Acid (HCl)	Removes inorganic metallics.
Hydrofluoric Acid (HF)	Removes inorganic resists, other organic materials and oxide films.
Hydrogen Peroxide (H_2O_2)	Chelating agent which removes inorganics left by acids also relieves the hydrophobic nature of films so acid solutions can penetrate.
Nitric acid (HNO_3)	Removes inorganic resists and other organic materials.
Nitrogen (N_2)	Used to dry the wafer and atomize the chemistry.
Peroxymonosulfuric Acid ($\text{H}_2\text{S}_2\text{O}_8$)	Removes resists and other organic materials.
Sulfuric Acid (H_2SO_4)	Removes inorganic resists and other organic materials.
Trichlorethylene (TCE)	Removes organic resists.

Source: VLSI RESEARCH INC
2245-122W

second bath is the same as for the first one. This bath removes inorganic contaminants.

Another sequencing clean is the FSI clean. FSI cleans employ the same chemicals in somewhat different proportions optimized for spray applications. The FSI SPM:HF treatment uses sulfuric-acid and hydrogen peroxide (4:1) followed by HF. This is equivalent to a 'piranha' resist strip followed by an oxide deglaze. The FSI 'APM' treatment—hydrogen peroxide and ammonium hydroxide (2:1)—is a counterpart to the

RCA 'SC1' clean. The FSI 'C' clean uses hydrogen peroxide in conjunction with ammonium hydroxide and hydrochloric acid. Here, the chemicals equate to an RCA, SC1 and SC2 series. HF may be added in the FSI clean as an oxide deglaze. Finally, the FSI 'B' clean is then chemically equivalent to the 'full RCA clean' previously described.

Several methods are used during wet cleaning. They are bath immersions, (ultrasonic or megasonic agitated immersion methods), brush and jet scrubbing, and spray cleaning.

All of these techniques remove foreign particles from the wafer. After the wafer is cleaned, it is rinsed in DI water and spun or IPA vapor dried. Two alternative cleaning techniques which have emerged are vapor phase cleaning and dry cleaning. These techniques use little or no wet chemicals. These cleaning processes are performed during various stages of wafer manufacturing operations.

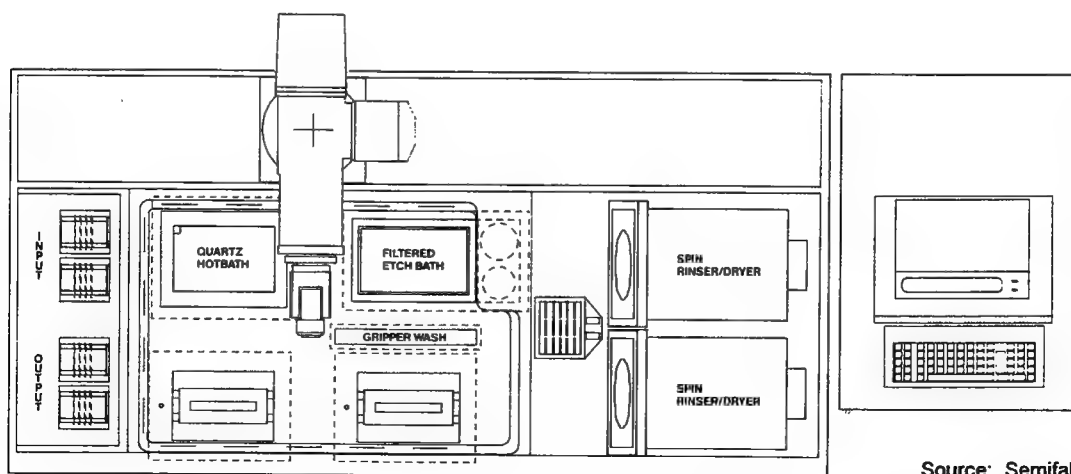
Bath Immersion Methods

More often than not, wet clean methods use some sort of immersion method. Immersion in liquid baths serves as a means for putting the reagent in intimate contact with the surfaces. It is commonplace in cleaning. Typical immersion cleans in semiconductor processing provide surface preparation for subsequent processing and for the removal of process by-products.

Immersion baths are usually found in a wet station. These stations can be used for cleaning, wet stripping or etching. Various options or features can be displayed in a wet station (see presentation 4.7.1.2.4-4). Some of the options available include:

- Agitation (water boat movement, bubbled nitrogen, magnetic stirrers, ultrasonics, megasonics),
- Recirculation and filtration,
- Cascade, spray or quick dump rinsers,
- Spin rinsers and dryers,
- Bath temperature controllers,
- Liquid level controllers,
- Resistivity monitors,
- Bath timers,
- D.I. hand spray and nitrogen guns,
- Auto transfer,
- Instrumentation (time, temperature and transfer recipes).

Two immersion methods of cleaning use ultrasonic or megasonic energy. Ultrasonic cleaning systems use sonic energy of 20 KHz and above to dislodge particles. In this system, the high-intensity sound waves generate pressure fluctuations that result in cavitation bubbles. As the bubbles collapse, the energy released removes particles. Megasonic cleaning systems removes particles by a high-pressure wave mechanism. The name "megasonic" refers to any ultrasonic scrubbing action greater than 80 KHz. A typical megasonic scrubbing action is pro-



Source: Semifab
2245-55

Presentation 4.7.1.2.4-4

A Typical Wet Processing Deck

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vided by piezoelectric transducers operating at 750 KHz to 1 MHz. A megasonic cleaning system is shown in presentation 4.7.1.2.4-5.

Scrubbing Methods

Scrubbing systems use the shear forces of other fluids, usually DI water, to remove particles. There are two general categories of scrubbers. They are brush and fluid jet scrubbers. Brush scrubbers use physical brushes, either cylindrical or round. Cylindrical brushes are more common. The brushes are usually made of nylon or polypropylene. In a brush scrubber system, the wafers are placed in a vacuum chuck. The brush scrubber is positioned close to the wafer surface, while the vacuum chuck rotates in the opposite direction. In this method, DI water fills the gap between the wafer and brush. So the brushes do not actually touch the wafer surface. This combination creates a high-energy cleaning action (see presentation 4.7.1.2.4-6).

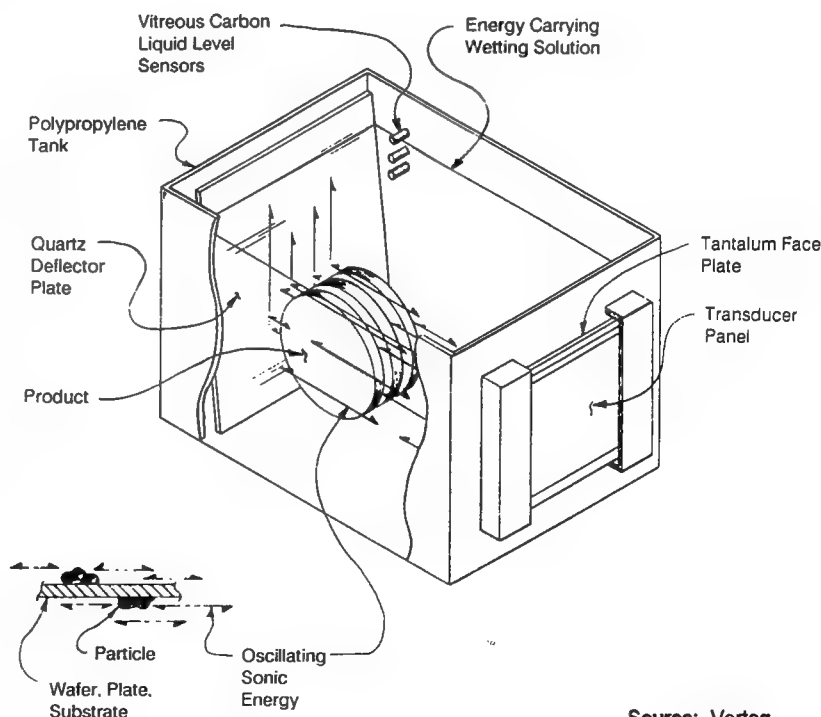
Brush scrubbers are excellent for removing stubborn particles larger than 1 micron from a hydrophilic wafer surface. However, problems with secondary contamination could arise if the brushes and the cleaning liquids are not kept clean. In addition, if the brush height above the wafer is not adjusted correctly, scratching of the wafer surface could occur.

High pressure jet scrubbing uses a high velocity jet of liquid to sweep over the wafer surface and remove contaminants. The most common liquid used is DI water. Usually a small amount of surfactant is added to the water

stream. This mixture acts as a destatic agent. Pressures up to 4000 psi are generated. This high pressure method penetrates dense topography, forcing the removal of particles.

Spray Cleaning Methods

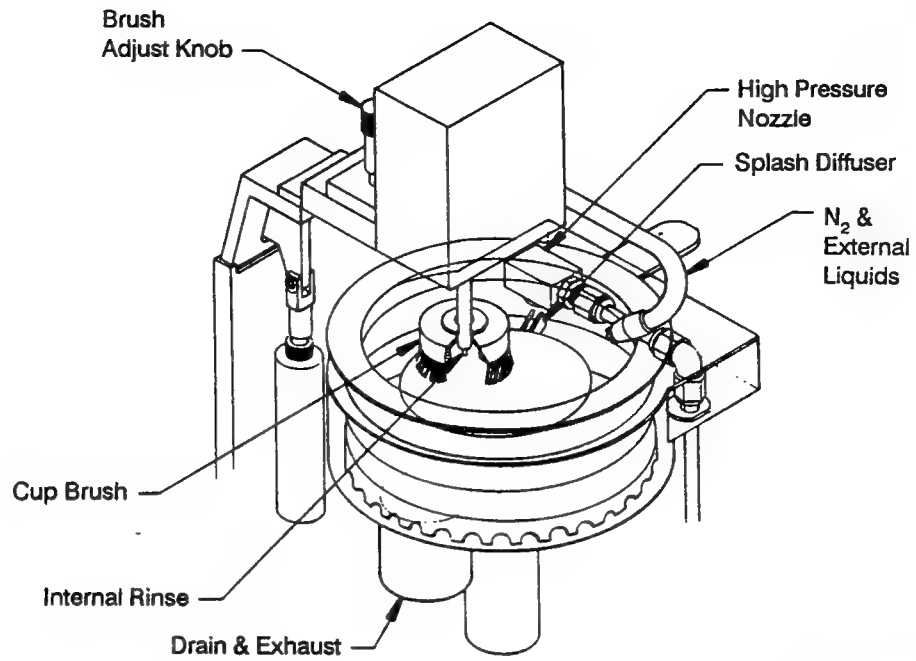
Spray cleaning is another method of cleaning wafers. With spray cleaning systems the liquid is sprayed through a post which is permanently positioned in the center of the chamber (see presentation 4.7.1.2.4-7). The wafers are cleaned as they are rotated past the spray column while liquid sprays out. The advantage of the system is there is no potential brush contact to the wafer surface. In addition, the fluid can penetrate recesses too small for a brush. The disadvantage is that the forces required to dislodge particles approach forces at which product damage can occur.



Source: Verteq
2245-52

Presentation 4.7.1.2.4-5

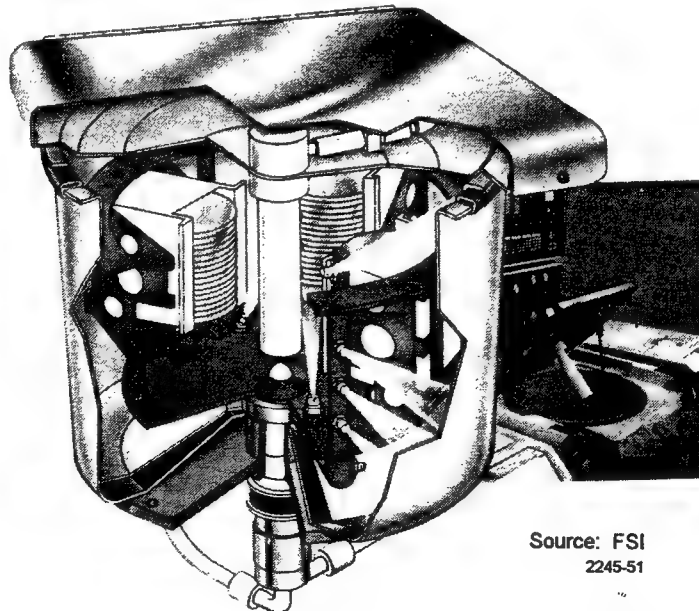
A Megasonic Cleaning System



Source: Solitec
2245-50

Presentation 4.7.1.2.4-6

Brush Scrubber Architecture



Source: FSI
2245-51

Presentation 4.7.1.2.4-7

Spray Cleaning System

Rinsing and Drying Methods

Once the wafers have been cleaned they must be rinsed and dried. This process reduces particulate and metal ion contamination that is inherent in wafer processing. Rinsing and drying are important steps. They ensure the longevity of all the benefits achieved in the previous cleaning surface treatments.

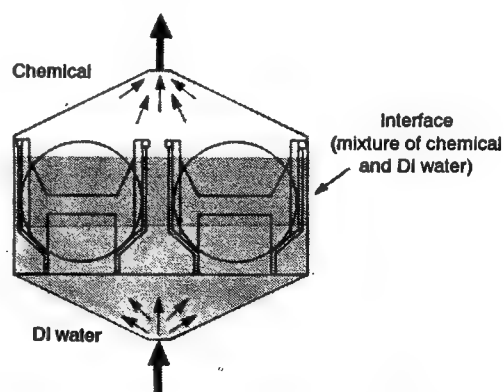
Spinning or centrifuging is a standard method used in rinsing and drying wafers. These systems are constructed of teflon or other types of clean material to reduce particulate contamination. Rinsers and dryers that use centrifugal force have a drum type configuration. With this method, wafer boats are placed in holders around the inside surface of the drum. In the center of the drum is a pipe with holes that is connected to a source of DI water and hot nitrogen. The center pipe sprays water on the wafers as the drum starts to rotate. Heated nitrogen is then sprayed into the drum once rotation increases. The heated nitrogen assists in the removal of small droplets of water that remains on the wafer. The drum spins at speeds up to 5000 rpm with minimal vibration. This centrifugal force physically removes water from the wafer surfaces. A disadvantage to spin rinsing and drying systems is the re-contamination of particles and aerosols due to the mechanical motion.

Another method for drying the wafers is by vapor drying. Vapor drying methods eliminate the mechanical motion that is associated with spin rinsers and dryers. Instead, the wafers are dried by a solvent vapor. Typically, the chamber of a vapor dryer is constructed of a formulated silicon carbide material. This single wafer chamber consists of two hemispheres and a center ring. The single wafer configuration eliminates cross-contamination which can occur in batch systems. The wafer is contained vertically inside the chamber. The solvent vapor, usually isopropyl alcohol (IPA), is

transported to the chamber by an argon or N₂ carrier. This vapor solvent displaces the water on the wafer surface. As the wafers are removed from the system, the vapor quickly evaporates since it is highly volatile.

The advantage of vapor drying over spin rinsers and dryers is there are a small amounts of particles left on the wafer. This is because there is no mechanical motion in a vapor system. Another advantage is less chemicals are used. However, the use of isopropyl alcohol is the main drawback due to the safety hazards involved and the disposal of the chemical.

CFM Technologies developed a chemical processing system that uses an IPA vapor displacement technique for drying wafers in an enclosed chamber. Enclosing the IPA vapor in the chamber eliminates potential human contact with the hazardous vapor. Initially, the wafers are rinsed in DI water. The wafers are then dried by an IPA vapor. The last step uses nitrogen to remove the IPA from the vessel housing (see presentation 4.7.1.2.4-8). The advantages of CFM's system include the static environment of the wafers, the elimination of gas to liquid interfaces and a fully automated system.



Source: CFM
2245-53

Presentation 4.7.1.2.4-8

CFM's Full-Flow Vapor Dry System

Capillary drying is another method for drying wafers. This method uses the capillary action and surface tension of DI water to dry the wafers. The idea behind the DI flow pattern is to remove particles that are on the top of the surface of the bath mixture. An advantage of this method is re-depositing particles are eliminated. In addition the static build-up of a hot dry nitrogen that occurs in a spin rinser and dryer is also eliminated. The concern over this method is the problems that can arise by using hot water which is an aggressive solvent. Even with evaporation, there is the possibility of residues being dissolved in the water which will be transferred to the wafer surface after drying.

Alternative Cleaning Methods

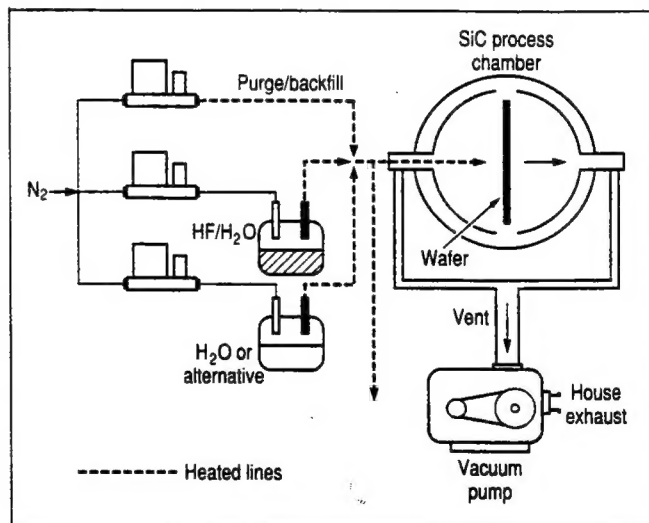
Consumption of chemicals during wet processing has increased due to the increase in wafer diameter. Concerns of wet chemical wastes' effect on the environment is bringing about the need to reduce or eliminate wet chemicals. Therefore, demand for cleaning processes which require little or no wet chemicals has increased. Vapor phase and dry cleaning technologies are two technologies that reduce or eliminate the wet portion of the cleaning procedure. Vapor phase and dry cleaning manufacturers have developed these technologies as cluster tool modules with single wafer capabilities. However, both technologies still need a wet rinse to remove all particle contaminants.

Vapor cleaning reduced the need for wet chemicals used in cleaning, rinsing and drying of the wafer. It also has advantages over plasma drying as there are no polymer residues. Within a vapor clean system, a solution of HF/H₂O or HCl/H₂O is heated to form a vapor. The vapors are then transported to the reaction chamber by an N₂ or argon carrier (see pre-

sentation 4.7.1.2.4-9). The main advantages to vapor cleaning are its uniformity and its ability to reduce metallic contamination. It has proved particularly useful in precleaning for contaminant sensitive processes such as tungsten.

A variety of dry cleaning methods are being investigated. One method uses a UV-excited gas technique to clean the wafers. This process uses UV light to photo-dissociate contaminants from the wafer surface. Once the contaminants are detached, they are trapped and scrubbed away by an inert flowing gas.

Another method uses carbon dioxide snow. With this method high-pressure carbon dioxide gas is blown through a nozzle, causing the gas to expand. The pressure drops due to the CO₂ expansion and the temperature reduces. As a result, solid carbon dioxide particles are formed. These particles bombard the wafer surface. However, the purity of the CO₂ seems to be incompatible with silicon wafers. Therefore, it is not generally used for silicon wafers.



Source: Advantage
2245-54

Presentation 4.7.1.2.4-9

Schematic of a Vapor Cleaning System

A third dry cleaning method uses a low energy DC gas discharge in an argon or hydrogen atmosphere to remove contaminants.

4.7.1.2.5 Other Wet Processing Technologies

Other wet processing equipment includes non-wafer related cleaning equipment such as mask, quartz and container cleaners. However, this equipment is indirectly related to the wafer manufacturing process. The cleanliness of the mask, the quartz parts in the equipment and wafer containers are important in retaining the cleanliness of the wafers.

The contamination of masks and reticles occurs in several forms. Particulate contamination is most prevalent. Other forms of contamination are organic residues, dry spots, fingerprints and condensation. Various methods are used to clean masks and reticles. One method is to spray the masks with detergent, scrub them with brushes, rinse with D.I. water and dry them with nitrogen. Another method, involves brush scrubbing with a cleaning solution, immersing in an ultrasonic vibrating bath and then drying with IPA vapors. The cleaning solution contains solvent degreasers and surface active detergents, i.e. surfactants. Mask inspection follows the cleaning. Inspection systems are usually incorporated in mask cleaning systems. A third method is to first clean with acid, rinse with D.I. water, then clean with detergent, rinse with D.I. water again, then dry with IPA vapor.

Equipment contributes a considerable amount of particulate contamination during semiconductor manufacturing. Anywhere from 25% to 39% of all particulate contamination originates with processing equipment.

The techniques used today to clean equipment include acid immersions, spraying, sonic agitation, rinsing and wiping.

One of the most frequently cleaned parts of equipment are quartz tubes and bell jars which are used in diffusion, CVD and sputtering processes. These quartz parts are required to be exceptionally clean during wafer processing. Before cleaning, the tubes and jars are first removed from the equipment. They are then cleaned with an acid wash, rinsed with D.I. water and finally dried by hot nitrogen air. There are three types of quartz cleaners. They are vertical, horizontal and bell jar quartz cleaners.

One tube cleaning technology that came and went was Benzing Technologies' AutoClean 10. The Autoclean 10 was designed for in-situ cleaning of diffusion/CVD tubes. It used a reactive plasma to remove polysilicon, silicon nitride and other materials from diffusion/CVD tubes. This technique was introduced in 1985. However, it had a five year lifespan, at most. One obvious limitation of the plasma in-situ cleaning technology was its inability to remove heavy and transition metals. Removing the heavy and transition metals required a wet clean.

Containers used to process and transport wafers need cleaning as well. The majority of wafer carrying containers are made of perfluoroalkoxy (PFA) fluoropolymers. PFA is considered to be pure, chemically inert and thermally stable. However, PFA carriers can be a source of wafer-surface contamination. PFA is a soft material. It abrades easily at contact points. So friction between wafer carrier and wafer, particularly at the carrier slots, can create particles. These particles can then be transferred to the wafer surface. Thus, the biggest problem with the containers is knowing if the containers are clean. The second biggest problem with the containers is cleaning them.

Container cleaning is accomplished mostly by automated cleaning methods. These cleaning methods consist of a high pressure DI-water jet spray, combined solvent and spray wash, brush, or ultrasonic cleaning. After the containers are cleaned, they are then rinsed with DI water and either spun or blown dried. Cleaning methods such as DI-water spray or brushing induces static charges on the PFA surfaces. These static charges generate a very high voltage which attract particles. This creates a possibility of contaminating the wafer. One method of cleaning which has been developed to coun-

teract this static charge is to use isopropyl alcohol (IPA) in the cleaning process. IPA properties prevents particles from being attracted to the PFA surface. This method uses a centrifugal jet spray of IPA/DI water to physically remove particles without inducing static charges. Carriers are then spun dried in the same chamber. The IPA centrifugal jet spray cleaning method appears to be a very effective cleaning method. Since the surface tension of IPA is much weaker than water, IPA rapidly wets carrier surfaces so particles are flooded and easily removed by centrifugal force.

Notes